

DEVELOPMENT AND PERFORMANCE OF FIXED BED CHLORINATOR

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**in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY**

By
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to the
DEPARTMENT OF CIVIL ENGINEERING
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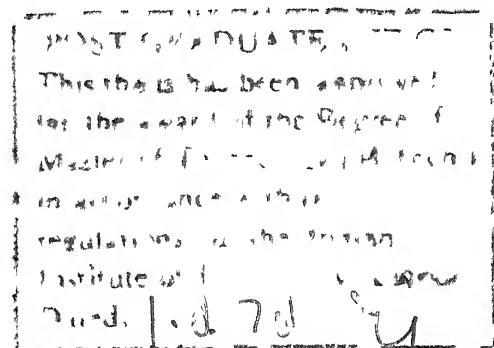
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CERTIFICATE

Certified that the work presented in this thesis entitled 'Development and Performance of Fixed Bed Chlorinator' by Shri Shirishkumar M. Sadekar has been carried out under my supervision and it has not been submitted elsewhere for a degree.

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DEVELOPMENT AND PERFORMANCE OF FIXED BED CHLORINATOR

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ABSTRACT

A simple self regulatory, easily operated, and maintained disinfection filter was developed in the present study. Out of four solid supports used to develop fixed bed disinfection column only urea melamine formaldehyde (UMF) resin was found to be suitable both from the point of adsorption and subsequent disinfection. However, all four supports namely UMF-resin, De Acidite-N resin, Weakly anionic resin supplied by CSMCRI, Bhavnagar and Chitin showed good potential for absorbing chlorine.

The column containing 1.8 g of chlorinated UMF-resin could easily be operated at loading rate of 540 lpm/sq.m. which is 3.4 times more than rapid sand filter. At this rate the column produced about 200 litres absolutely sterile water before start of breakthrough of E. coli. The effluent water contained the residual chlorine concentration in the range of 0.6 to 0.8 mg/l which takes care of post

contamination. Chlorine release from the column appeared to be function of flow rates adopted, the higher flow rates resulting in lower residual chlorine release and vice versa. Further, turbidity present in influent water does not seem to have significant effect on chlorine release.

The disinfection data obtained for various loading rates follow the Chick's model of disinfection with slight deviation. It appears from the data presented that chlorinated UMF-resin has great potential as water disinfectant particular for our rural areas where instalation of chlorine dosing and regulating equipment along with their operation and maintenance is impracticable. This process also can find wide applications in isolated urban areas, in railway compartments etc.

CHAPTER - 1

INTRODUCTION

Water, whether or not previously filtered and even if perfectly clear, is often contaminated by microbes dangerous to human health. Among others, pathogenic bacteria and enteric viruses form a considerable fraction of water contaminants and are solely responsible for causing the water borne diseases. The provision of safe water is the prime objective of water treatment and anything less in this regard is unacceptable.

Water treatment processes, such as, sedimentation, coagulation, filtration etc. are helpful in the removal of other contaminants along with a fraction of microbes, but, are certainly inadequate as far as the provision of safe water is concerned. Water is considered safe only when it is completely free from pathogenic bacteria and enteric viruses. Disinfection is the only unit process that ensures total destruction of pathogenic organisms and safeguards us against various water borne diseases. Complete eradication of water borne diseases in many countries and particularly in U.S.A. (Jenkins, 1963; Reid and Carlson, 1974) amply support this statement. Further, in recent times, people all over the world have become so conscious about pollution in general and the quality of potable water in particular, that there

is hardly any need to plead for supply of disinfected water.

At the end of 1970, the rural population of the developing countries surveyed by W.H.O. amounted to 72 percent of the total population of those countries. Of these rural population, 86 percent were without 'reasonable access to safe water' (World Health Statistics Report, 1973). In India also 80 percent of the masses are living in villages where construction of organised water supply schemes becomes financially difficult. Nevertheless, it is essential to ensure that most of these people get atleast microbially safe if not completely treated water.

Further, in our country there is a continuous and large movement of people from one place to another. This contributes significantly to the spread of diseases, particularly water borne diseases. The water supplied to these people, therefore, needs to be properly disinfected.

Even in those areas where we have got organised water supply it is desirable and customary to maintain a certain residual concentration of disinfectant in water to account for any possible contamination in the distribution system. The inadequacy of such residual disinfectant is often noted in many cities because of poor maintenance of distribution systems and the long journey undertaken by water in reaching

the consumer's end. Hence, it is essential to regain the original quality of water by adopting disinfection at the consumer's end.

In many parts of our country ground water is the main source of domestic water, and in most cases this water meets the water quality standards laid down in the Indian Manual on Water Supply and Treatment (1976), just by adopting disinfection.

Chlorine as compressed gas in liquid form is almost universally employed for the disinfection of municipal water supplies. Chlorine gas is difficult to handle unless special equipment is available from which it can be dispensed. Hence its usefulness in the gaseous state is limited to only large scale operations such as water treatment plants where it is possible to install suitable equipment for safe handling. This makes the task of providing disinfected water to rural areas, isolated colonies, railway compartments, and even to some parts of the urban population, a difficult job as the conventional method of disinfectant injection is not suitable in such cases because of high cost and technical complications involved.

Under these circumstances it is natural for an environmental Engineer to think of some other cheap,

suitable and simple disinfecting technique which can be used in lieu of the conventional one.

1.1 Objective and Scope of the Study

The present work was initiated with an aim to develop a fixed bed disinfectant which would supply disinfectant on demand obviating the complications involved in conventional disinfecting practice.

Keeping in mind the above aim, a search was made for various possible solid supports which would take up disinfectant when kept in disinfectant rich environment and would release the same in disinfectant deficient systems.

A comparative study of various solid supports with regard to their suitability in terms of adsorption of disinfectant and performance in terms of inactivation of bacteria was conducted.

Solid supports: Following solid supports were used.

(1) Anion Exchange Resins

- (a) Urea-Melamine-Formaldehyde (U.M.F) resin.
- (b) De Acidite N - a strongly basic anion exchange resin supplied by Ion-Exchange (India) Ltd.
- (c) Weakly basic anion exchange resin supplied by Central Salt and Marine Chemicals Research Institute, Bhavnagar.

(2) Biological Material

(a) Crab shell Chitin

Disinfectant: Chlorine was used as the disinfectant.

Model Organism: In order to evaluate the performance of the fixed bed disinfectant in terms of microbial inactivation, Escherichia coli was used as the model organism.

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CHAPTER . 2

LITERATURE REVIEW

2.1 The Practice of Disinfection

Though the scientific and logical application of disinfection is only about 150 years old, ancient people were aware of the use of clean water and proper handling of waste material to ensure good health. Religious books like the Bible and the Vedas contain instructions on use of clean water. There is evidence that older civilization used to store drinking water in brass or copper containers before use (Weber, 1972). The great scientist and philosopher Aristotle had instructed his king Alexander to supply boiled water to the army and bury their waste (Block, 1968).

In 1825, for the first time chlorinated lime was used to prevent the infection of wounds. Dr. Robley Linningser (White, 1972) in his book 'Human Health', published in Philadelphia in 1835, suggested the use of chlorine to make the water of marshes potable. Later in 1846, Semmelweis introduced chlorine water as an antiseptic to prevent the spread of child bed fever (White, 1972) in a Vienna general hospital.

This early use of chlorine for disinfection was based on the erroneous assumption that odours spread infection (Iaubusch, 1971). Fortunately, chlorine's

oxidising property which was responsible for the removal of odour strengthened this belief. It was not until mid-1860's when the germ theory of disease was finally established that an inkling was gained into how diseases actually spread.

The first recorded observation of wide spread transmission of disease by a public water supply relates to the 1854 London cholera associated at the Broad street well. This was followed by serious outbreaks of typhoid fever in Lausen, Switzerland, in 1872; outbreak of cholera in Hamburg, Germany in 1892; and several other serious outbreaks of epidemics in U.S.A., in the last decade of the 19th Century (Weber, 1972). On investigation it was found that in all these cases the cause of outbreak was contaminated water. In the meantime, Pasteur, in 1863, had developed the germ theory of disease, and, Robert Koch, in 1881 was able to demonstrate the destruction of pure culture of bacteria by hypochlorite under controlled laboratory conditions.

Harrased by the severity of water borne diseases and encouraged by the findings of above workers, people started thinking in terms of obtaining pure water for the purpose of drinking. Around 1897, Kruizing and Paul carried out research work which laid the foundation of modern chemical disinfection (Block, 1968). Madsen and Nyman, and Chick, later in 1910, proposed mathematical models for

the action of disinfectant which gave the people a better understanding of the process (Benzac et.al., 1967). This chain continued, and till to date several researchers have worked in the area of disinfection and have contributed significantly to the knowledge of people.

Disinfection of domestic water as a continuous process was first adopted at Middlekerke, Belgium, in 1902, when chlorine was used for this purpose (White, 1972). After that gradually it spread in other countries and today this process has become an integral part of water treatment systems.

2.2 Various Disinfectants used in Water and Waste Treatment other than Chlorine.

Besides chlorine there are several other disinfectants which are used in water and waste water treatment. Important among them are ozone, bromine, iodine, chlorine dioxide, surfactant, silver ions, ultraviolet irradiation and ultrasonic vibration. However, the usage of these disinfectants is very limited as compared to chlorine.

Nevertheless, the use of chlorine has the following drawbacks which has prompted the search for new disinfectants:

- 1) Water containing phenol results in the formation of chlorophenolic compounds which produce taste and odour

problems.

- ii) Chloramines and organic chloramines formed as a result of reaction with ammonia and protein present in water or wastewater have questionable viricidal activities.
- iii) More recently, the formation of chloroform, a potent carcinogenic compound, due to chlorination of water, has significantly drawn the attention of Environment Engineers (Harris, 1974; Bellcr, et.al., 1974; Gerba et.al., 1977).
- iv) Possibility of formation of chlorinated organics photochemically by sunlight in waters being disinfected by chlorine (Oliver and Carey, 1977) has caused concern among environmental engineers.
- v) Waste water containing chlorine residuals, whether free or combined, affect the ecology of aquatic environment (Brungs, 1973; White, 1972; Selleck and Collins, 1974).

All these possible short-comings of chlorine have led to the call for the development of alternate disinfectants. The nearest competitor to chlorine as a disinfectant for potable water is ozone. Problems like taste and odour and formation of chloramines are eliminated by the adoption of ozonation (Kellar,et.al., 1974, McCarty and

Smith, 1974, Kuo and Chian, 1977). Chlorine dioxide is another compound which can be used for disinfecting water containing high concentration of ammonia and phenolic compounds (Morris, 1970; Augenstein, 1974). The advantages of its use are similar to that of ozone.

Bromine, Br₂, is a dark reddish brown halogen that exists as a liquid at atmospheric pressure and is less cumbersome to handle than compressed gas. It is slightly soluble in water and has got a good germicidal action. As is the case with chlorine, amino forms are produced in the presence of ammonia and other trivalent nitrogenous materials. Bromine and monobromamine have been reported nearly equal in bactericidal properties and essentially equal to free chlorine on a part-per-million basis at comparable pH (Johnson and Overby, 1971). Applications of bromine appear to be limited to the treatment of swimming pools and industrial waters. With the use of bromine there is an apparent reduction of eye irritation and its odours are not troublesome.

Iodine also is more common in disinfecting swimming pools since unlike chlorine it does not irritate the eye (White, 1972). Though the disinfecting efficiency of iodine is less than that of chlorine, it is preferred to chlorine in disinfecting water being supplied to remote areas or in developing countries where little or inadequate

supervision and expertise are available (White, 1972). As the tendency of iodine to form objectionable organic substitution compounds is much less than that of chlorine, post disinfection with iodine provides longer lasting protection against pathogens and alleviates the problem of offensive tastes and odours often caused by chlorine. Because of its limited activity, less iodine is usually required to obtain a desired free residual. Another advantage with iodine is that both I_2 and its hydrolysis product, HIO , are equally good disinfectants.

Among surfactants, the cationic detergents are strongly destructive, the anionic detergents are weakly so. The neutral detergents occupy an intermediate position. These detergents are more common as disinfectants in the waste waters and rinse waters of eating establishment (Fall, et.al., 1968). Encouraging results on water disinfection were obtained by Wang and Perry (1975) and Prasad (1977) using quaternary ammonium compounds.

It has been known for many centuries that copper is bactericidal (only weakly so) and strongly algicidal. Other metals, such as mercury and silver, are also notably effective in minute concentrations. Silver is a soft lustrous, white metal that is insoluble in water and alkalies. It is

readily ionised by electrolysis, and this property is the basis for some systems used in the disinfection of water. In addition, it can also be applied as a solution of its salt or by desorption from filter beds of silver coated sand, carbon, fabric etc. (Weber, 1972). However, its usage till now is limited to small water supply installations, food industry and carbonated beverages industry.

Use of other physical disinfectants like ultraviolet irradiation and ultrasonic vibration are limited to disinfect very small quantities of water. Their cost of installation puts them off the list of possible disinfectants in developing countries.

2.3 Disinfection of Water and Wastewater by Chlorination

In the previous article a comprehensive evaluation of other possible disinfectants along with their limitations has been made. But the popularity which chlorine enjoys is unparalleled. It is so because chlorine possesses all the qualities required for an ideal disinfectant in an optimum manner (White, 1972). Other agents may equal or even exceed aqueous chlorine in any one of the qualities, but there are none that combine them in such an advantageous way. As a matter of fact, of all the municipal water supplies that are being chemically disinfected, at least 99 percent

use chlorine (Morris, 1966). Further, the research done with other disinfectants is very less as compared to chlorine and as a result the side effects associated with other disinfectants are not fully known.

In this regard the following observation of Editor of Indian Association for Water Pollution Control (Raman, 1973) is interesting to note: 'Much is talked about the long term ill effect of chlorination on humans due to the possible formation of carcinogenic compounds (halo-organics) in presence of certain organics. There is some evidence in USA and in the West. Nearly 400-500 chloro organic compounds have been identified of which all are not carcinogenic. In this controversy, the beneficial and immediate effects of chlorination of water in the control of enteric diseases both in the developed and developing countries during the past four decades seem to have been overlooked. In developing countries including India, chlorination of water shall have to continue to be the means for disinfection of public water supplies since enteric diseases are still endemic in these regions. The technical and financial resources in developing countries are very much limited as to practise alternative disinfection procedures. Dr. Morris of Harvard University rightly feels that chlorine will continue as the major disinfectant for drinking water'.

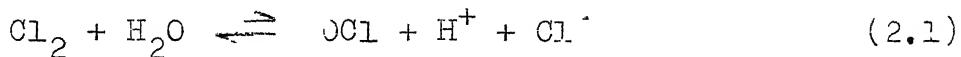
2.3.1 Chlorine

Chlorine is the second most reactive element of the halogen family, but is never found uncombined in nature. It is estimated to account for 0.15 percent of the earth's crust in the form of soluble chlorides, such as common salt (NaCl), carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$), and sylvite (KCl). However, there are few known natural organic compounds containing chlorine (Fowden, 1968). In nature, therefore, it exists only as the negative chloride ion with a valence of -1. It was first discovered by Karl W. Scheele a Swedish Chemist, in 1774 and later proved to be an element by Davy, in 1810. It has an atomic number of 17 and an atomic weight of 35.457. Molecular chlorine, Cl_2 , has a weight of 70.914. Two isotopes of chlorine, Cl^{35} and Cl^{37} , occur naturally, and ordinary atomic chlorine consists of a mixture of about 75.4 percent Cl^{35} and 24.6 percent Cl^{37} . It usually forms univalent compounds, but can also combine with a valence of 3, 4, 5 and 7 (White, 1972).

2.3.2 Chemistry of Chlorination

Chlorine is used in the form of free chlorine or as hypochlorites. In either form it acts as potent oxidising agent and often dissipates itself in side reactions so rapidly that little disinfection is accomplished until

amounts in excess of chlorine demand have been added (Sawyer and McCarty, 1967). With pure water chlorine combines to form hypochlorous and hypochloric acids (Morris, 1946; Connick and Chia, 1959)



The hydrolysis constant $K_H = 4.48 \times 10^{-4}$ molcs/lit. at 25°C.

The hypochlorous acid formed is a weak acid and is very poorly dissociated at pH levels below 6.



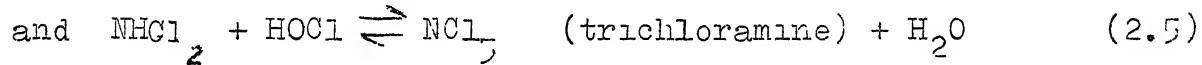
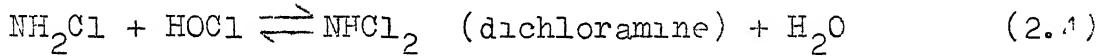
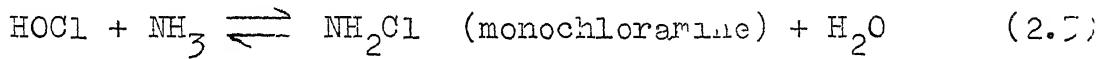
The ionization constant $K_1 = 2.7 \times 10^{-8}$ moles/lit. at 20°C.

The presence of molecular chlorine (Cl_2) is restricted only to a pH value below 3.0 and at concentrations above 1000 mg/lit. (Reid and Carlson, 1974). In dilute solution and at pH levels above about 4.0, the equilibrium shown in equation 2.1 is displaced greatly to the right. It is obvious that the relative amounts of OCl^- and HOCl present in the solution, is a function of pH and temperature.

The most important and undoubtedly the most complex chemistry of water and wastewater chlorination is its reaction with various forms of nitrogen naturally occurring

in water. If there were no nitrogenous compounds present in water, probably there would not have been any trouble of tastes and odour due to chlorination. Further, there would not have been any problem of the quantitative differentiation of chlorine as most of the chlorine applied would have been in the free form (White, 1972).

Chlorine in aqueous solution reacts with ammonia in the following manner (Griffin and Chamberlin, 1941).



As a result of these reactions with increasing dose of chlorine applied, there is a sudden loss of free chlorine with simultaneous disappearance of ammonia. This observation led many investigators (Fair, et.al., 1947; 1948; Morris, 1946; Morris et.al., 1948, and Palin 1950, 1950a, 1950b) to the discovery of breakpoint chlorination which ultimately gave us the modern concept of chlorination.

Above paragraph deals with reaction of chlorine with inorganic or ammonia nitrogen. The chlorine reaction with organic nitrogen, particularly proteins and amino acids, is even more complex. In proteins and amino

acids there are several potential sites of reactivity with chlorine. Chlorine can react with either the N-terminal or the peptide amino nitrogen to form organo-chloramines or products of further reactions. Hence the chlorine demand curve obtained in the presence of organic nitrogen is not as well defined as in the presence of inorganic nitrogen (Weber, 1972).

2.3.3. Mode of Action of Chlorine

The process of disinfection is not instantaneous. Certain minimum dose of disinfectant and a minimum time of contact between the disinfectant and the organisms is required. In addition, the nature of disinfectant, temperature, pH, and the nature and concentration of microorganisms also play a vital role (Fair et.al., 1968). Consequently, after being so much in use, the exact mode of action of chlorine in 'killing' microorganisms is not yet known (White, 1972). Furthermore, little is known about the number of chlorine molecules required to kill a single microorganism (Weber, 1972). However, one thing is certain that a series of physical, chemical and biological steps are involved in the inactivation of microorganisms (Weber, 1972).

The earliest scientific concept of microbial inactivation by nascent oxygen, liberated by the decomposition

of hypochlorous acid has been more or less discarded now. Eventually newer theories of disinfection are being developed. Green and Stumpf (1946) suggested that the death of bacterial cells results from a chemical reaction of HOCl with an enzymic system essential to glucose oxidation and cellular metabolism. Later these workers (Knox et.al., 1948) demonstrated that the death of cell is due to oxidation of sulphhydryl groups of the vital enzymes. Ingols et.al. (1953) supported this theory but concluded that this mechanism of inactivation is only limited to vegetative cells. Wyss (1962) has noted that destruction of part of an enzyme system throws the cell out of balance causing the death before any repair mechanism acts to revitalise the enzyme. More recently, Venkobachar (1975) and Venkobachar et.al. (1977) reported significant inhibition of both oxygen uptake and oxidative phosphorylation by chlorine. The latter effect was attributed to the inhibition of the appropriate respiratory enzymes, rather than to a deficiency of phosphate uptake.

2.4 Fixed Bed Disinfection

Literature on fixed bed disinfection is scanty. There is no information as yet on implementation of such a method in practice. The prominent works contributed in this field are by Taylor et.al. (1970); Dewar and Wayman (1972); and

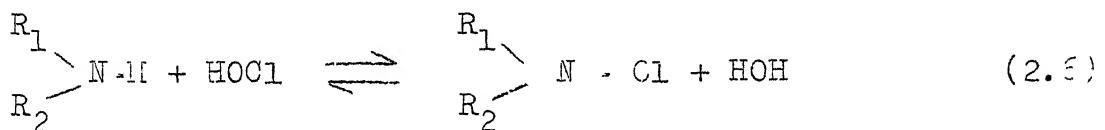
Fina and Lambert (1975). Out of the 12 workers the work done by Taylor et.al. (1970) and Fina and Lambert (1975) is on development of fixed bed disinfectant using iodine as the disinfectant and the contributions of Dewar and Wayman is a similar effort using chlorine as the disinfectant.

Paterson (1969) developed a method of disinfecting water in which water flows over preformed solid agglomerates containing N-halogenated compounds. It is capable of releasing controlled amounts of bromine or mixtures of bromine and chlorine into water. The agglomerates are formed by mixing N-halogenated compounds with some powdered matrix material like sodium silicate, aluminium hydroxide or zeolite along with water and then drying it.

Schneider et.al. (1970) proposed a chlorine releasing material which was prepared by mixing and pressing alkali or alkaline earth metal hypochlorites with sodium stearate and moulding it in the form of a hollow cylinder. The disintegration of material occurred due to the flow action of water.

Wayman et.al. (1968) had prepared high polymers which contain a labile chlorine atom. The active group in these polymers is the --NH_2 or --NH_2 group, which takes up chlorine from a chlorine rich environment and in the chlorinated form

gives up chlorine to an environment deficient in chlorine, for example which exhibits a chlorine demand. The resin, which may be natural or synthetic, acts as an agent for chlorine transfer to or from a medium as per following equation



Later Dewar and Wayman (1970; 1971; 1972) further studied on the formulation of solid base, the diffusion of chlorine in it and its possible use as fixed bed chlorinator.

Taylor et.al. (1970) developed a fixed bed disinfectant by complexing triiodide ions with strongly basic anion exchange resins. This combination has remarkable antibacterial properties. 3×10^5 E. coli cells per ml. were killed (residence contact time = 12 sec.) when passed through a 1.8 cm. long and 1.8 cm. dia. column containing charged resin. Later, working on similar columns, Fina and Lambert (1975) found that even the water sample charged with virus became sterile when passed through columns of resin-triiodide complex. It is claimed by these investigators that iodine is supplied by resin on demand.

Kreusch and Husseini (1973) got their process patented for treating contaminated water by iodine treated activated carbon. In this process iodine is reversibly absorbed by activated carbon used in filtering beds. The carbon bed releases free active iodine when water is passed through it. The exhausted bed is regenerated by passing iodine solution through the bed.

Svilkovsky and Hofer (1973) have developed a small cartridge filter capacity 0.5 to 2.5 m³/hr) which removes colloidal particles, excess chlorine, unpleasant odours and taste, and, in addition, can induce bactericidal activity to water in a single run. The filter contains a mixture of activated carbon with cotton, asbestos, and (or) cellulose coated with silver. The filter material is jacketed by cellulose ester films of pore diameter less than 0.5 microns on cardboard support. The exchangeable cartridge is placed in a sealed cylindrical filter body.

CHAPTER - 3

MATERIALS AND METHODS

3.1 Materials

3.1.1 Escherichia coli

E.coli was chosen as model organism in all the experiments to study the disinfecting behaviour of chlorine charged solid supports. Factors, viz., ease in handling, easy to distinguish, easy to grow, and its sanitary significance led to the selection of the above organism.

3.1.2 Organism and Media

The pure stock culture of E.coli was obtained on agar slants from National Chemical Laboratory, Poona.

Various media used for bacteriological work were as follows:

(a) Medium for growth of E.coli

Beef Extract	3 g
Sodium Chloride	5 g
Peptone	5 ..
Distilled water	1 litre
pH adjusted to 7.2 with 1 N NaOH.	

using Systronics pH meter.

(b) Slants for subculturing E. coli

Beef Extract	3 g
Sodium Chloride	5 g
Peptone	5 g
Agar	20 g

pH adjusted to 7.2 with 1 N NaOH using
Systronics expandometric pH meter (I/S. Systronics , Ahmedabad).

(c) Medium for enumeration of E. coli

Peotone	10 g
Lactose	10 g
Dipotassium hydrogen phosphate	2 g
Eosiny	0.4 g
Methylene blue	0.065 g
Agar	15 g
Distilled water	1 litre

pH adjusted to 6.9 ± 0.1 with 1 N NaOH.

3.1.3 Sterilization

Media and dilution water (tap water) for plating were sterilised in pressure cooker at 15 psi pressure (121°C) for 15 minutes. Other glass wares like petridishes, pipettes, bottles for sample collection etc. were sterilized in hot air oven at 200°C for 2 hours.

3.1.4 Preparation of Bacterial Culture

From a 24 hours old slant culture a loopful of E.coli was inoculated in 100 ml sterile medium (a). This was agitated at 37°C in a wrist shaker for 8 hours to obtain a culture in log growth mode by dipping the lower portion of conical flask in controlled temperature water bath.

3.1.5 Preparation of Test Water

For preparing test water containing desired concentration of bacteria tap water was used. It was confirmed that the tap water was free from residual chlorine before use. A known volume of bacterial suspension obtained as described in Section 3.1.4 was added to a known quantity of water free of residual chlorine, such that the initial bacterial concentration of the test water was in the desired range. The test water was stirred using a laboratory stirrer so as to homogeneously disperse the bacteria.

3.1.6 Preparation of Chlorine Solution

Chlorine solution was prepared by bubbling chlorine gas through distilled water which was made slightly alkaline (pH approx. 9.0) by adding 1.0 N NaOH. For preparation of chlorine gas concentrated hydrochloric acid was added to potassium permanganate crystals.

Chlorine solution thus prepared was kept in an amber coloured glass bottle and was stored in a refrigerator. The pH of this solution was in the range of 3.5 ± 0.5.

The strength of stock solution decreased considerably with time and hence the strength was measured accurately before starting each experiment.

3.1.7 Solid Supporting Bases

Various solid bases used in the experiments were

- (i) Urea-Melamine-Formaldehyde resin prepared in the laboratory.
- (ii) Strongly basic anion exchange resin, De Acidite N - a product of Ion Exchange (India) Ltd. under licence from the Permutit Co. Ltd., London.
- (iii) Weakly basic anion exchange resin supplied by Central Salt and Marine Chemicals Research Institute, Bhavnagar.
- (iv) Crab shell chitin
 - (a) Prepared in laboratory out of fresh water crabs obtained from some local fisherman.
 - (b) Prepared in laboratory out of marine water crab shells supplied by Merrers M.K. Fisheries, Cochin (Kerala).

(c) 'Chitin pract'. supplied by Koch-light Laboratories Ltd., Colnbrook-Bucks-England.

3.1.7.1 Preparation of Urea-Melamine-Formaldehyde Resin

The resin was formulated in the laboratory after modifying slightly the method suggested in the book 'Preparative methods of polymer Chemistry' (Sorenson and Campbell, 1963).

In a 250 ml round bottom flask equipped with a condensor was placed a mixture of 4.2 g (1.0 M) melamine, 2 g urea (1.0 M), and 25 ml. of 37 percent aqueous formaldehyde (3.4 M). The mixture was adjusted to a pH of 9-10 by the addition of 1.0 g sodium carbonate, refluxed in water for 3 hours, then acidified at 80°C with 4 ml of concentrated hydrochloric acid. On acidifying the colourless syrup immediately turned into a white opaque mass. It was air-dried overnight at 60-65°C and then ground to obtain a particle size as required. Before using for experimentation the resin was washed with 1.25 N sodium hydroxide solution.

3.1.7.2 Preparation of Crab shell Chitin

Dead crabs were kept in water for several days after which they were taken out and dried fully under sun. This loosened the shells and they were peeled out of crab. Shells were again dried thoroughly and were crushed into

fine powder. About 200 gms of this powder was then taken in a 2 litre beaker and dilute hydrochloric acid (about 6 N) was added to it slowly. Care was taken to avoid spillage .. due to foaming on the side of the beaker (Herning,1962). This reaction mixture was then allowed to stand overnight to enable complete removal of calcium carbonate. Residual was then filtered and washed with water until it was neutral to litmus. It was then dried in hot air oven at 50-60°C. The material thus obtained was brownish-yellowish in colour. To decolourise it 6 N Potassium hydroxide was added to it and the mixture was kept in bath for 4 hours. The material was again dried before use for experimentation.

3.2.. Methods

3.2..1 Chemical Composition of Test Water

The test water consisted of tap water to which bacterial suspension was added. The chemical composition of tap water in terms of parameters like hardness, alkalinity pH, conductivity, and chloride was evaluated according to 'Standard Methods for the Examination of Water and Waste Water'. Hardness and chloride were estimated by EDTA titrimetric method and Argentometric method respectively, where as, conductivity was measured using Wiss.-Techn.-Werkstätten, Weilheim obb. Conductivity cell. A typical analysis for

tap water is presented in Table 3.1

Table 3.1
Composition of Tap Water

Parameters

i)	pH	8.3
ii)a)	Free residual chlorine	Nil
- b)	Combined residual chlorine	Nil
iii)	Conductivity	1.5×10^{-5} mhos/cm
iv)	Chloride	60.0 mg/lit as Cl^-
v)	Alkalinity	
a)	Methyl orange	440 mg/lit as CaCO_3
b)	Phenolphthalein	Negligibly small
vi)	Hardness	
a)	Total	240 mg/lit. as CaCO_3
b)	Ca^{++}	70 mg/lit. as CaCO_3

2.2.2 Determination of Chlorine and Residual Chlorine.

The chlorine, and the residual chlorine concentration in stock solution, in adsorption kinetics studies, in the effluents of column, or in batch studies was determined using DPD ferrous titrimetric method as given in Standard Methods (1976). As this method is very sensitive and is useful for determination of lower concentrations of

chlorine, the samples were diluted with chlorine demand free water as to bring down the chlorine strength of the solution around 0 to 4 mg/lit. range.

3.2.3 Evaluation of Chlorine Demand of Test Water

It is essential first to evaluate the chlorine demand of water to be disinfected in order to add appropriate dose of chlorine. Chlorine demand test for the test water used in the present investigation was conducted according to Standard Methods (1976). The standard contact time for the reaction used was 30 minutes. A typical chlorine demand curve for the test water is presented in Fig. 3.1.

3.2.4 Enumeration Technique for *Escherichia coli*

The enumeration of *E.coli* in the harvested suspension as well as the survivors after disinfecting action of chlorine was done by Standard plate count method using eosin methyleneblue agar (Standard Methods, 1976). The plates were incubated at 37°C for 24 hours before enumerating the developed colonies of *E.coli*.

3.2.5 Preparation of Disinfectant Solid Support

The disinfectant bed were prepared by adding known quantity of various solid supports, mentioned earlier, to different Corning bottles containing known

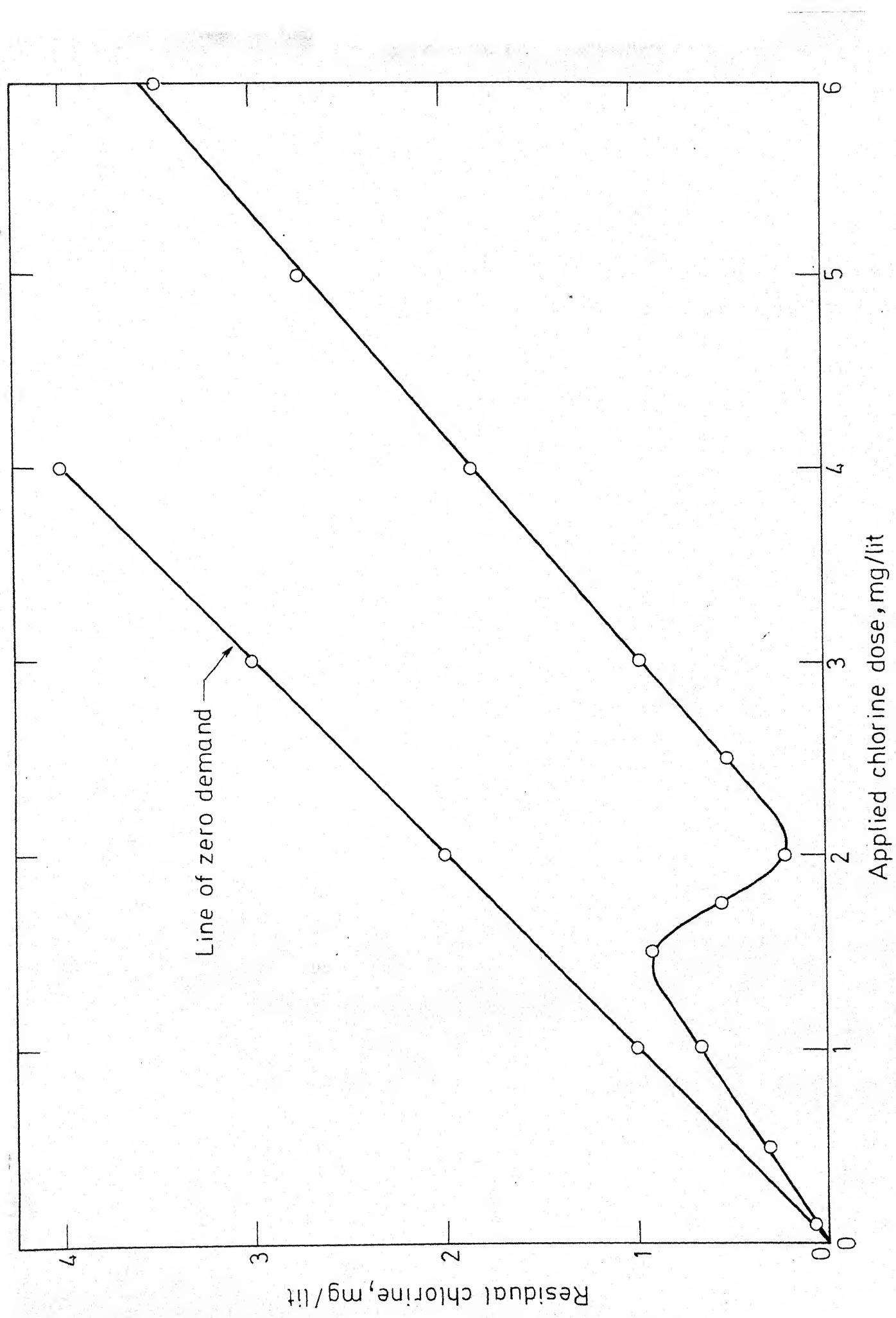


Fig.3.1 A Typical Chlorine Demand Curve for Test Water

concentrations of chlorine solution. To bring about better contact between solid support and chlorine solution the bottles were agitated in a rotary shaker. At different intervals of time samples were taken from the bottles and analysed for chlorine concentration in the supernatant. The experiment was discontinued when equilibrium was attained.

3.2.6 Disinfection Studies

3.2.6.1 Disinfection Studies in Batch Process

The batch studies on disinfection were conducted in a non-flow agitated reactor. The 500 ml bottle used as reactor was sterilized before starting each experiment.

For disinfection kinetics studies, a known quantity of charged solid base was taken in the above reactor along with a known concentration of bacteria suspended in sterile tap water (usually 250 ml). The reactor was agitated by a wrist shaker. 1 ml sample was drawn at each desired time interval and was neutralised with sodium thiosulphate before plating to enumerate the survivors. Simultaneous determination of residual chlorine concentration was not possible as the time interval were too small and also the method used for its determination required a large volume (100 ml) of sample. Yet to have an idea of chlorine residual

in the reactor the same test was repeated under same condition and samples were drawn only for residual chlorine determination at the same time intervals. At each time interval 25 ml of sample drawn was diluted to 100 ml and residual chlorine was estimated using DPD method. The reactor was replenished with 25 ml of distilled water after each withdrawl.

3.2 .6.2 Column Disinfection Studies

Column studies were conducted in a glass tube having an internal diameter of 0.75 cm. 1.8 g cf chlorine-charged resin was filled in the column (depth = 15 cm). The test water was passed through the column from a large size bottle (10 lit.). The particle size of resin chosen was such that it passed through I.S. sieve No. 36 (opening size = 0.425 mm) but was retained on I.S. sieve No. 72 (opening size = 0.212 mm) . Suitable arrangements were made to collect the influent and effluent samples from column for conducting bacteriological studies, and for determining the residual chlorine in the effluent. An average head of 4.0 feet was provided over the resin bed. The volume of test water (feed water) containing E.coli to be passed through the column was large and hence the test water was prepared using unsterilised tap water.

CHAPTER - 4

RESULTS AND DISCUSSION

Practical utility of any unit operation depends on explicit study of important parameters affecting the system. In the present investigation it is aimed to develop a fixed bed disinfectant by sorption of chlorine on to various solid bases and to use them subsequently in the form of fixed beds to disinfect the water. Hence the first step in this study is the adsorption of chlorine onto selected materials and the second step is to see their usefulness in the disinfection of wa...

4.1 Adsorption

4.1.1 Adsorption of Chlorine on UMF-Resin

Kinetics of adsorption not only describe the rate of solute uptake but also the mode of mechanism of the reaction at the equilibrium. Further, kinetics study helps to decide the contact time required between the solute and the sorbent for maximum sorption. Accordingly, sorption kinetics experiments were conducted and the results are presented in Fig. 4.1.

As is seen from the figure the time required to attain the equilibrium is of the order of 16-20 hrs and hence in all subsequent experiments the contact time provided was 20 hrs. The overall uptake rates are higher when the

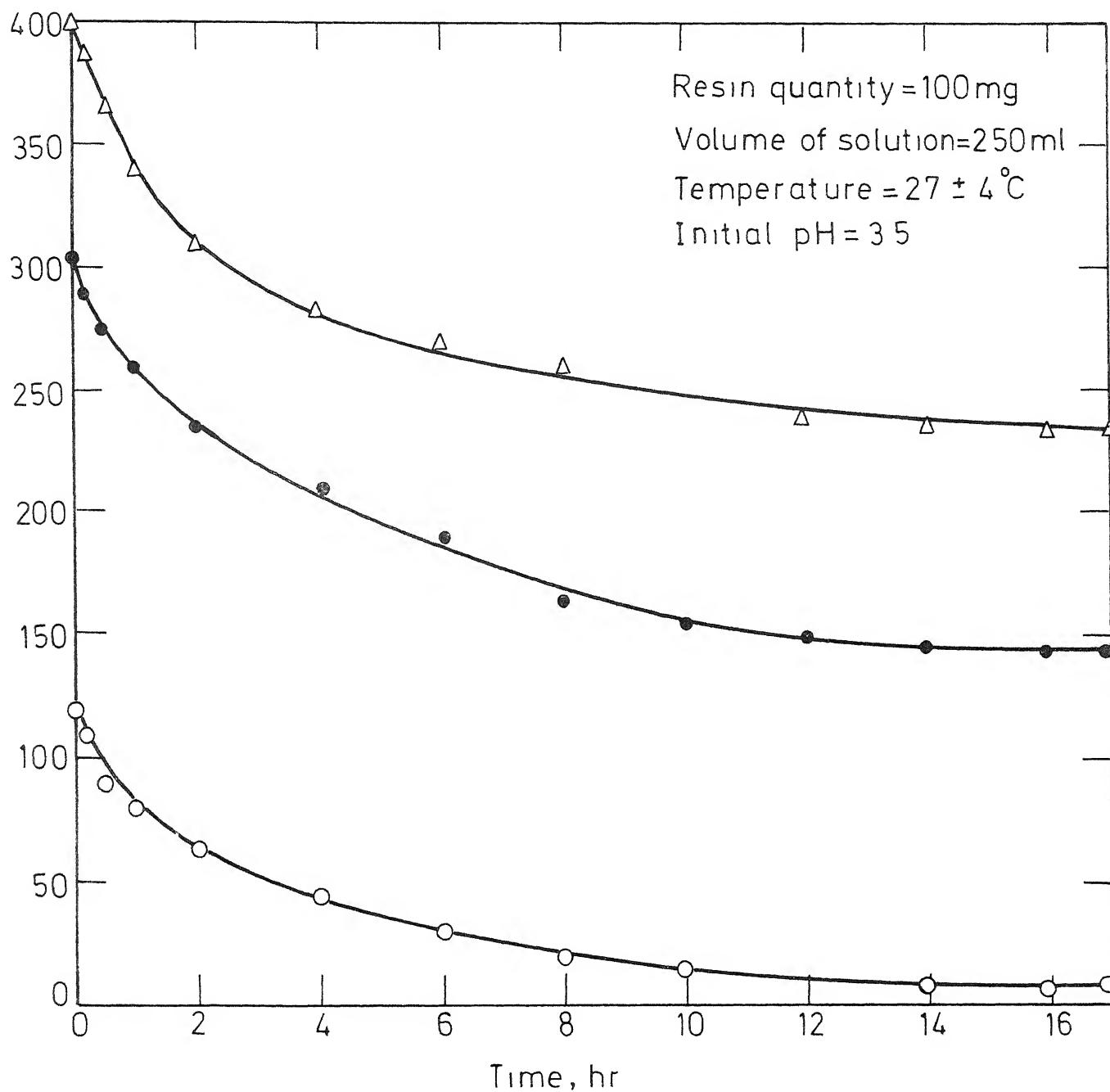


Fig 4.1 Kinetics of Chlorine Uptake by UMF-Resin

initial concentration of chlorine solution used is high.

The adsorption isotherm plotted (Fig. 4.2[a]) conforms to Langmuir isotherm. The equation is of the following form (Metcalf and Eddy, Inc., 1972)

$$\frac{X}{M} = \frac{abC_e}{1+bC_e} \quad (4.1)$$

where,

$\frac{X}{M}$ = amount adsorbed per unit weight of adsorbent.

a, b = empirical constants

and, C_e = equilibrium concentration of adsorbate in solution after adsorption.

The linearised plot of Langmuir isotherm for adsorption of chlorine on sorbent is presented in Fig. 4.2[b]. It follows the equation

$$\frac{C_e}{\frac{X}{M}} = 15 + 2.24 C_3 \quad (4.2)$$

Thus the emperical constants a and b for the present system are 0.445 and 0.149 respectively. As the adsorption data obtained is fitting Langmuir isotherm better than any

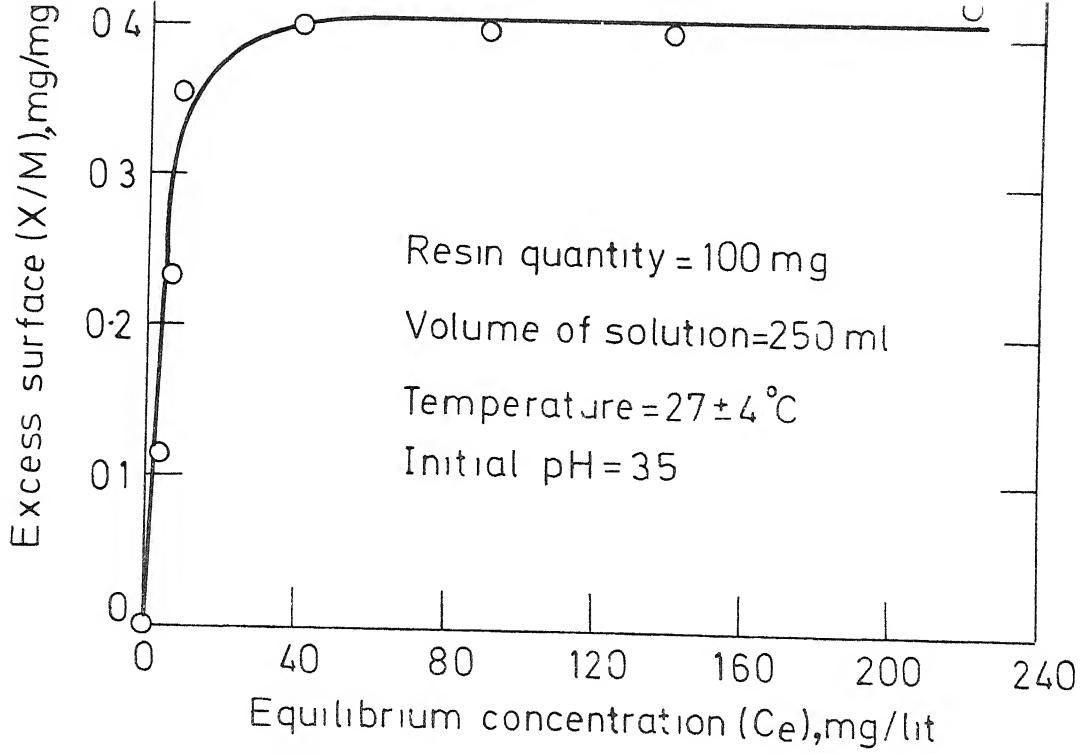


Fig 4.2(a) Adsorption Isotherm for Chlorine Uptake by UMF Resin

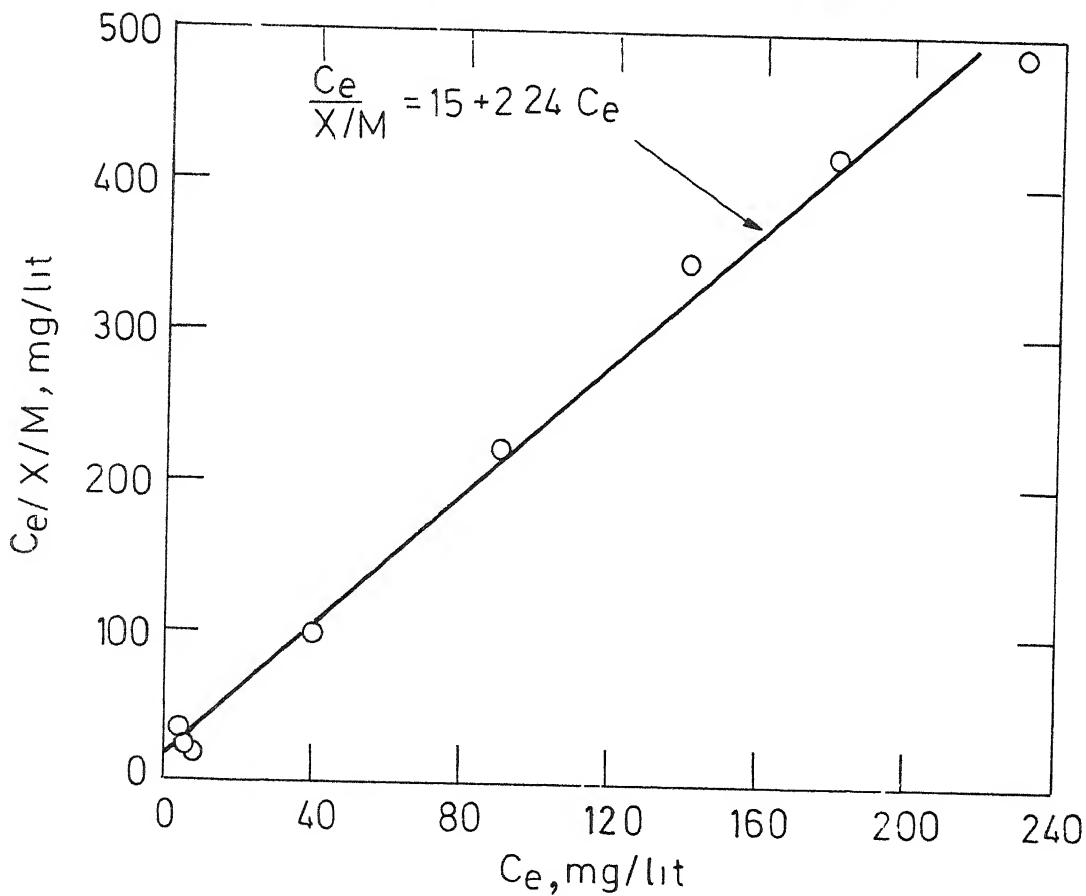


Fig 4.2(b) Langmuir Isotherm for Fig. 4.2(a)

other model, it can be said that the sorption of solute on sorbent is in single layer (Weber, 1972). According to Langmuir model maximum adsorption of solute on sorbent corresponds to a saturated monolayer of solute molecules on the surface. The saturation concentration of chlorine appears to be around 50 mg/lit. In all subsequent experiments regarding chlorine adsorption by resin, this concentration was employed. It can be further noted from Fig. 4.2 [a] that excess surface after adsorption is 40 percent.

Once the adsorption has taken place it is important to know the exact mechanism of adsorption, i.e. whether it is film diffusion or intraparticle diffusion. Theoretical treatment on the kind of diffusion yield rather complex mathematical relationships. However, a quick method to know the mechanism is to plot a graph between the sorbent uptake and the half power of time (Weber, 1972). Nearly linear variation of the amount adsorbed with $t^{1/2}$ is predicted for a large fraction of reactions controlled by rates of intraparticle diffusion. In the present study good linearization of the data is observed for the initial phase of the reaction, when such a curve is plotted. There is some deviation at the end of the run which may be due to appreciable change in the value of concentration gradient between the sorbent and the bulk as seen from Fig. 4.3.

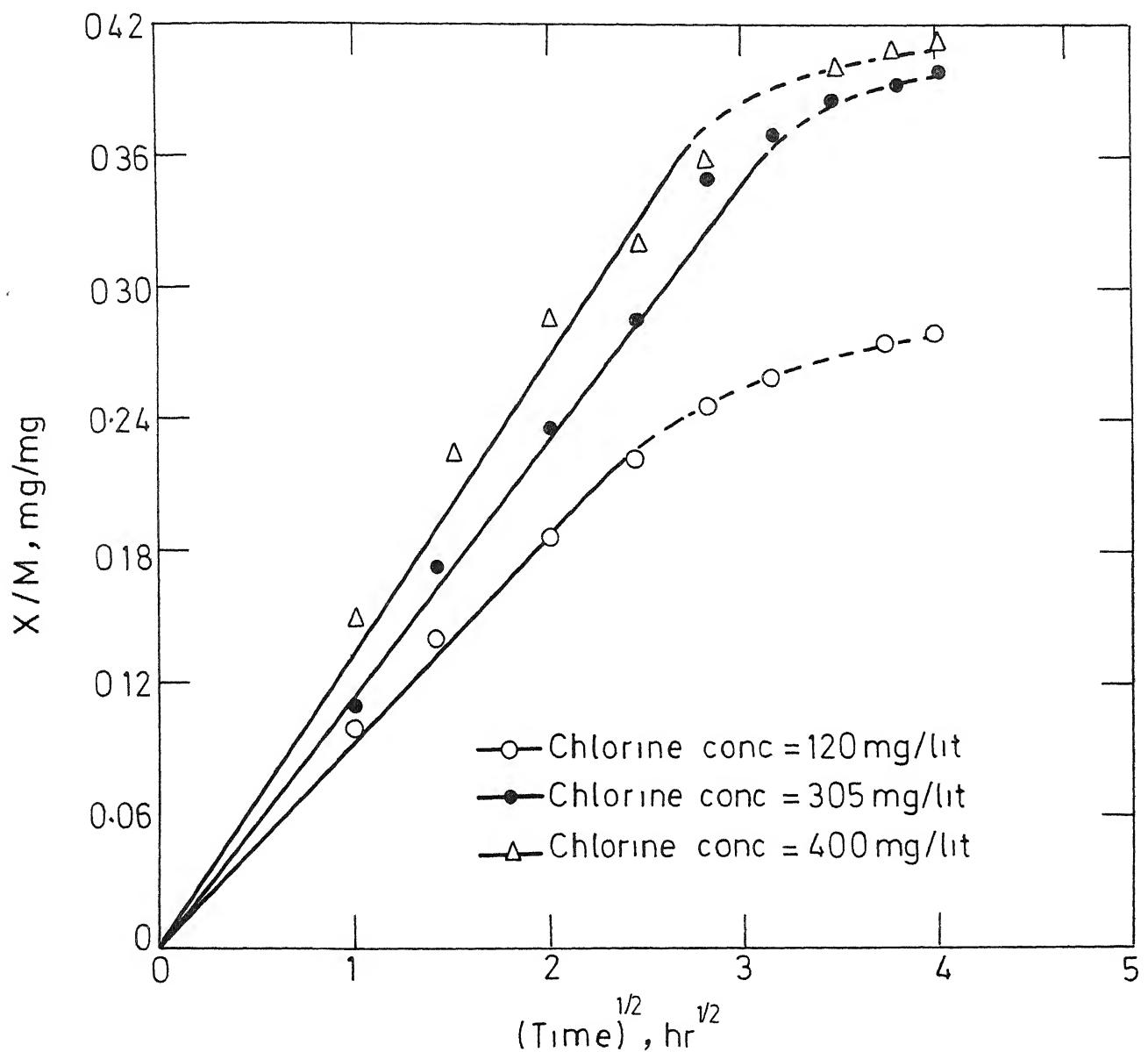


Fig. 4.3 Plot of Half Power of Time Vs Chlorine Sorbed for UMF-Resin

4.1.2 Adsorption of Chlorine on De Acidite-N Resin

The overall chlorine adsorption pattern of this resin does not appear to differ much from that of UMF-resin. The graphs for adsorption kinetics (Fig. 4.4), the adsorption isotherm along with its linearised form (Fig. 4.5 [a] and Fig. 4.5 [b]), and the adsorption mechanism (Fig. 4.6) are presented in the subsequent pages. However, the salient points in the adsorption process with this resin are given below:

(1) The equilibrium time in the present system is higher (24-26 hrs) than that of UMF-resin and hence the contact time required is more.

(2) The isotherm in this case also follows Langmuir equation. The saturation concentration is about 40 mg/lit as against 50 mg/lit in case of UMF-resin. As a result the excess surface developed is approximately 30 percent only.

(3) The empirical constants 'a' and 'b' of Langmuir model as obtained from Fig. 4.5 [b] are

$$a = 0.306, \quad b = 0.434$$

The corresponding equation of the straight line is

$$\frac{C_e}{M} = 7.5 + 3.26 C_e \quad (4.5)$$

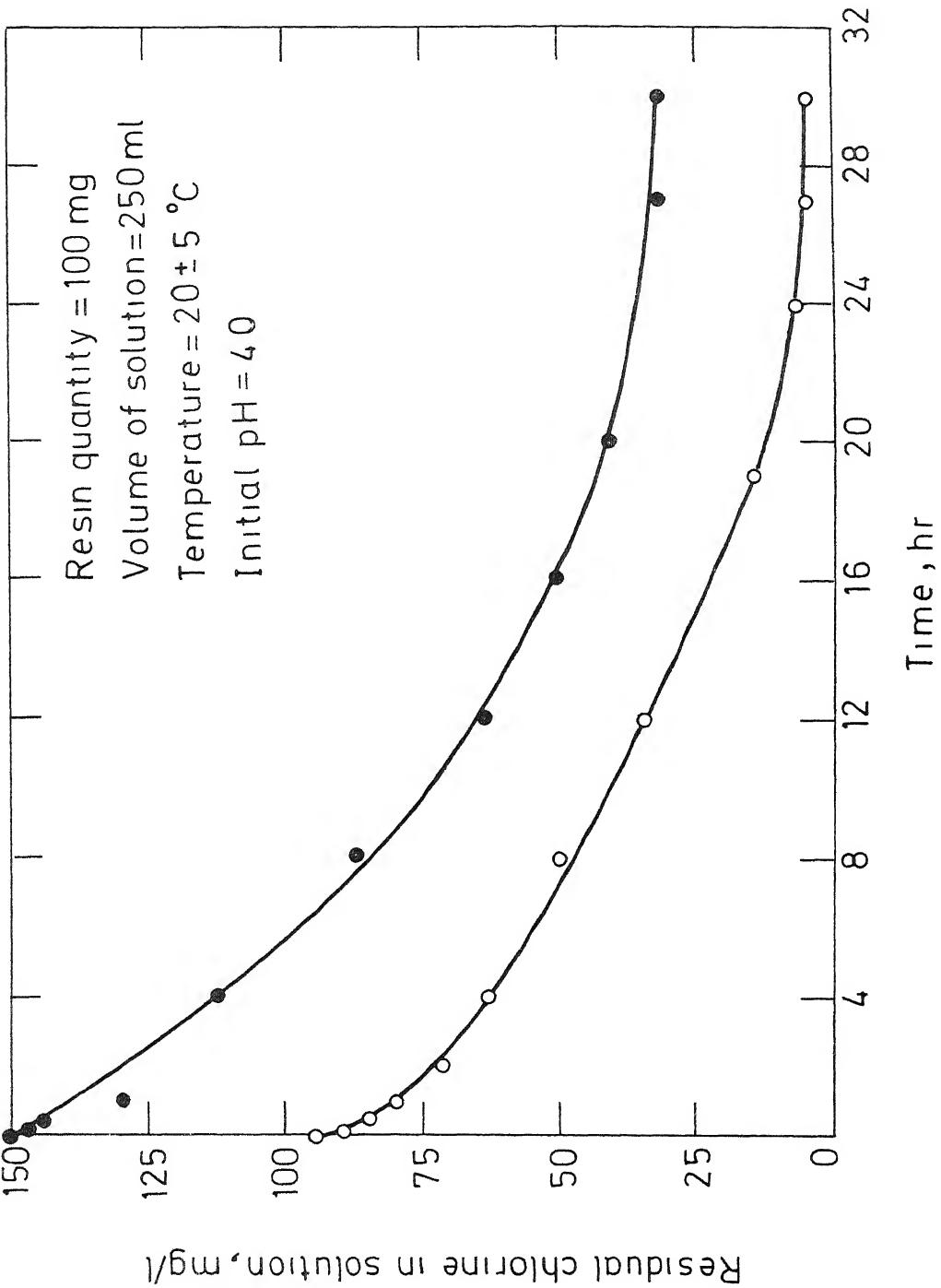


Fig. 4.4 Kinetics of Chlorine Uptake by De Acidite-N Resin

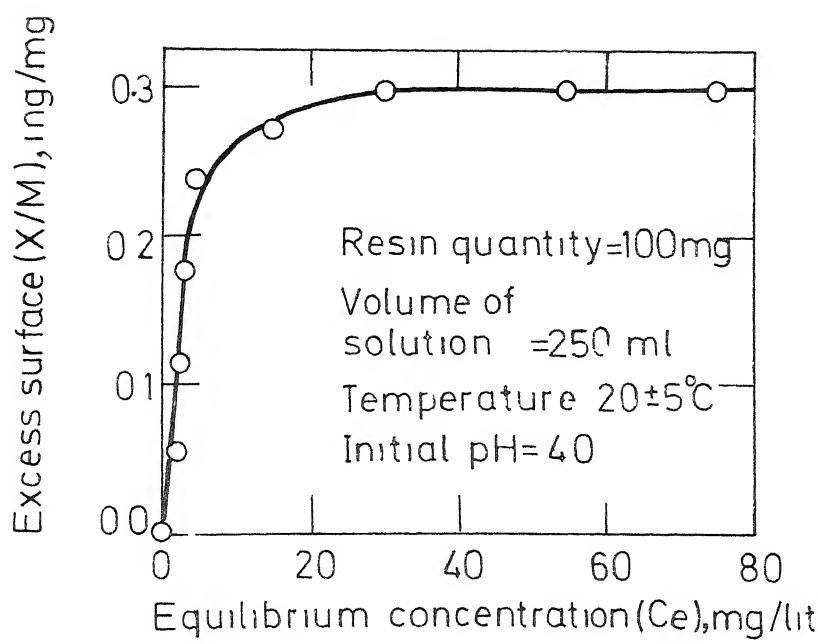


Fig 45(a) Adsorption Isotherm for Chlorine Uptake by De Acidite-N Resin

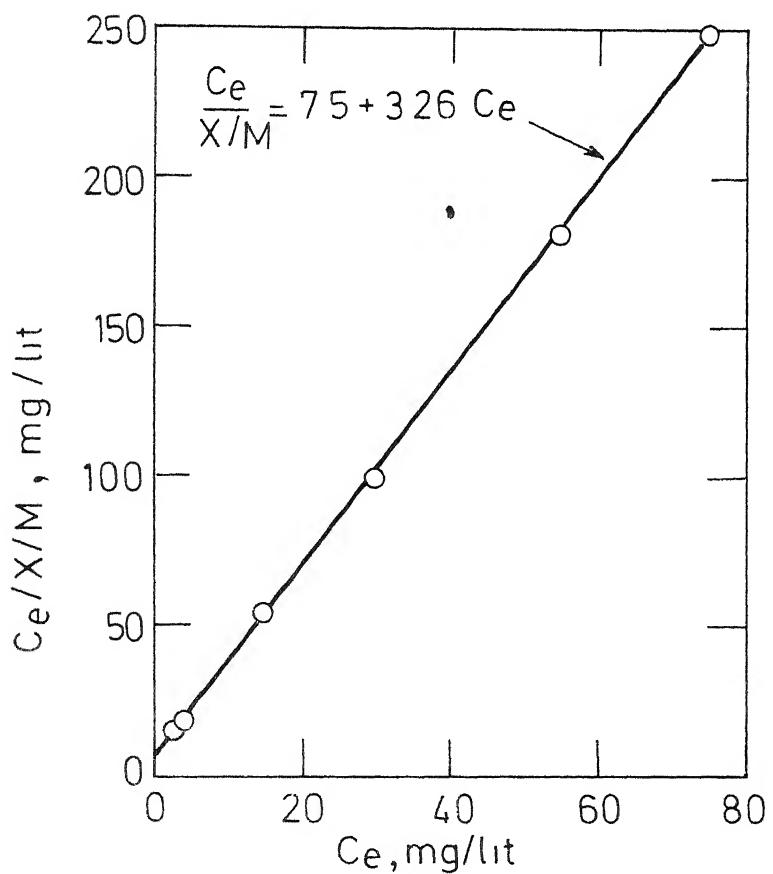


Fig 45(b) Langmuir Isotherm for Fig. 45(a)

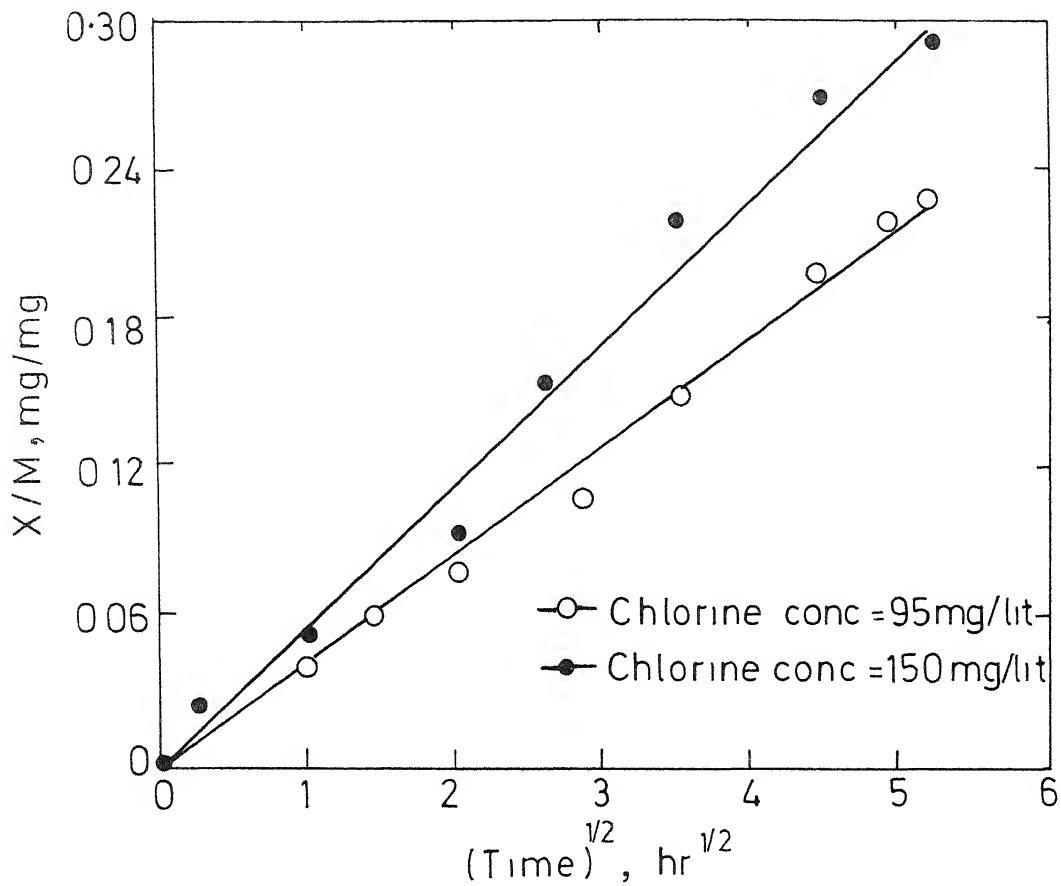


Fig 4.6 Plot of Half Power of Time
Vs Chlorine Sorbed for
De Acidite-N Resin

(4) The mechanism of adsorption is same as that in the case of UMF-resin.

4.1.3 Adsorption of Chlorine on Weakly Basic Anion Exchange Resin and Chitin

Sorption kinetics experiments similar to those described in the previous section, were conducted using a weakly basic anion exchange resin and chitin. Almost similar results were obtained with these materials also. The results are not presented here since their usefulness for disinfection was limited as found out in the following section.

4.2 Disinfection Studies in Batch Process.

4.2.1 Batch Disinfection Studies with UMF-Resin

In order to evaluate the disinfection properties of the chlorine charged urea-melamine-formaldehyde resin, preliminary batch studies were conducted. To a known quantity (0.5 g) of charged resin about 250 ml water containing *E.coli* concentration of the order of 2×10^4 number/ml was added and sufficient contact was provided by agitation in a wrist shaker. From this non-flow agitated system samples were taken out at different intervals both for determining chlorine release and bacterial survivors. Two different types of

systems in terms of turbidity were used and the results are presented below.

The chlorine release as a function of time both for clear and turbid water is presented in Fig. 4.7. It is seen that there is not much difference in chlorine release for these two systems. As there was not much variation in chlorine release it can be said that turbidity, at least upto 8 NTU, does not interfere with the desorption of chlorine from the resin. This may be because the pore size of resin is so small as compared to the turbidity particles that the turbidity particles are unable to block the pores. On the other hand, chlorine molecule, whose size is comparable to that of pore size, has got the backing of driving force arising due to concentration gradient existing between the sorbent and the bulk. This perhaps forces out the chlorine molecules in to the bulk. Further, the turbidity particles used were of non chlorine demanding, and inorganics. Consequently, the available chlorine in bulk in case of sample with turbidity and sample without turbidity was not different at different time intervals.

It is also seen from Fig. 4.7 that the rate of release of chlorine is high initially but tends to decrease slowly at the end of the run. Two reasons can be attributed

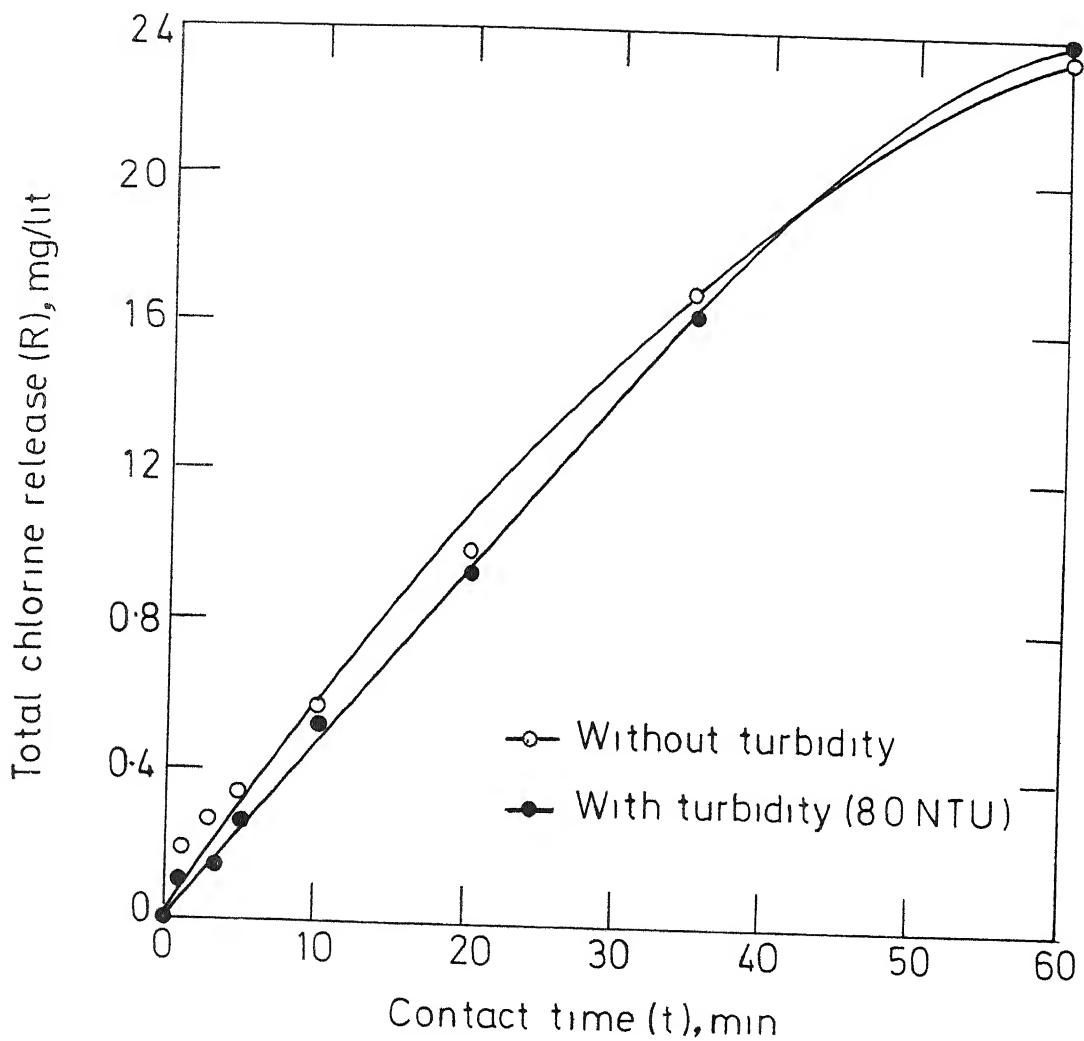


Fig. 4.7 Chlorine Release With Time for UMF Resin (Batch)

for this. Firstly, the concentration gradient which exists between the sorbent and the bulk decreases with time because of continued emergence of chlorine molecules into the bulk. Secondly, with the increase in contact time the chlorine demand of bulk reduces because of reduction in the oxidisable organic matter present in the form of E. coli.

The bacteriological data obtained both from clear as well as turbid water (8 NTU) is presented in Fig. 4.8. The plots are made according to Chick's disinfection model, namely,

$$\frac{dN}{dt} = -KN \quad (4.4)$$

where, N = no. of organisms at time t

and K = disinfection rate constant to the base e.

The solution of above equation is of the form $N = N_0 e^{-Kt}$,

where, N_0 = No. of organisms at time $t = 0$.

The disinfection curve for clear water appears to follow the Chick's first order equation ($K = 2.83 / \text{min.}$) The disinfection curve for turbid water of 8 NTU does not appear to follow this model. Two rate constants are evident from this plot. The rate of disinfection is low ($K = 0.082 / \text{min.}$) upto 3 min. and afterwards the rate is high ($K = 1.35 / \text{min.}$). Fig. 4.7 indicates insignificant difference in

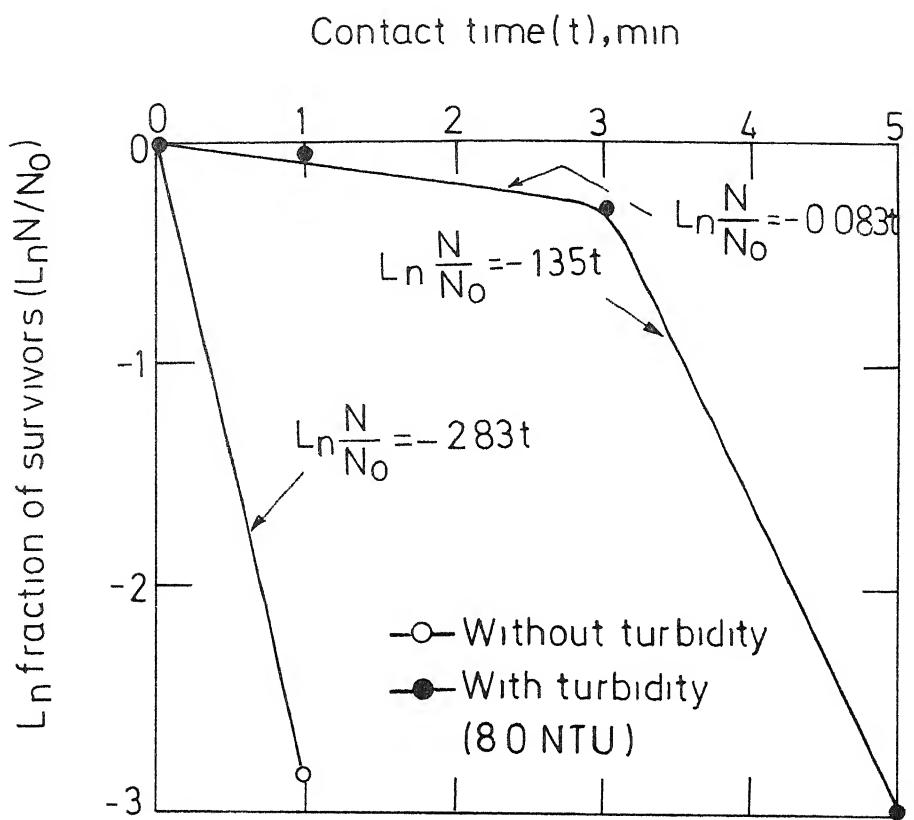


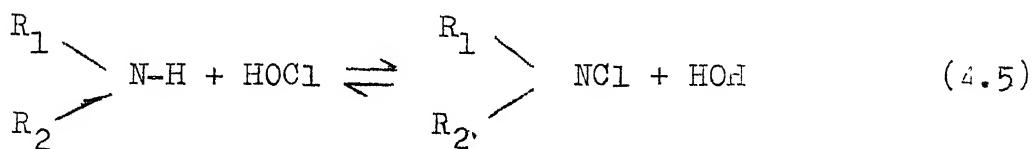
Fig 4.8 Chick's Model for Chlorine Disinfection with UMF-Resin (Batch)

chlorine release for clear and turbid water. However, the disinfection curves indicate significant variation in the two cases. This appears due to interference of turbidity with disinfection. Apparently the turbidity particles provide a sort of protection to the microorganisms against the action of released chlorine. While in clear water, the number of microorganisms decreased by 2 orders of magnitude in 1 minute, the decrease was insignificant even after 3 minutes in case of turbid water. Beyond 3 minutes, in case of turbid water, the chlorine release is also more and simultaneously the contact time has also increased. As a combined effect of both, the disinfection rate has also increased. On the basis of above results it can be inferred that in order to obtain the same disinfection efficiency in the presence of turbidity, the time of contact should be more or the concentration of released disinfectant should be more as compared to clear water.

It is interesting to note here that Chick's model is normally applied to a system in which a known concentration of disinfectant is added initially to water containing a particular number of microorganisms with the increase in contact time both, the number of microorganisms, as well as the concentration of disinfectant, decreases. As a result of this generally two rate constants for the

destruction of bacteria during disinfection of water or wastewater are observed. Initially a higher value of rate constant followed by lower value. On the other hand, in the present investigation the concentration of disinfectant increases with time because of more contact provided. The observation as per Fig. 4.8 for turbid water, indicates lower value of rate constant followed by higher value of it emphasising the combined effect of increased chlorine release as well as contact time.

The chlorine exchange reaction in the UMF-resin is possible because the resin consists of insoluble cross-linked polymers containing a large number of $-NH$ groups. These $-NH$ groups on the polymer react in the same way as those on isocynauric acid. They react with chlorine according to the reversible reaction:



The hydrogen is replaced by a positive chlorine. The equilibrium depends on the other groups attached to the nitrogen but generally the equilibrium favours the $NC1$ form. The reverse, hydrolysis, is the reaction that releases chlorine to the water (Dewar and Wayman, 1972; Wayman *et.al.*, 1968; Dewar and Wayman, 1970).

4.2.2 Batch Disinfection Studies with De Acidite-N Resin

In order to find out the suitability of using De Acidite-N resin in fixed bed disinfection, batch studies were conducted in similar fashion as described in section 4.2.1. The results indicate an altogether different trend. There was no release of chlorine from the resin showing that the chlorine is attached to the resin in an irreversible manner. De Acidite-N appears to act more like activated carbon in this regard than UMF-resin. Activated carbon absorbs chlorine but in an irreversible way and in the process the disinfecting properties of chlorine are destroyed by it (Kreusch and Husseini, 1973). Due to this property activated carbon is being studied by various investigators for dechlorinating water (Suidan *et.al.*, 1977). De Acidite-N resin may also find a similar application as activated carbon. Although De Acidite-N is an isoporous cross-linked polystyrene resin, unlike UMF resin the active group present on this resin is $-NR_3^+$. It is probably because of this tertiary amide group that the chlorine attached to this resin is in irreversible form.

4.2.3. Batch Disinfection Studies using Resin obtained from Bhavnagar.

The resin supplied by CSMCRI, Bhavnagar contains primary amide group (Dasare, 1978) and was also used to

evaluate its performance in terms of disinfection. Though the adsorption of chlorine by this resin was more than that of UMF and De Acidite-N resin, the disinfection data collected gave similar results as De Acidite-N resin. On this basis it can be said that this material also absorbs the chlorine irreversibly and in the process the disinfecting property of chlorine is destroyed. Because of rapid rate of adsorption, Bhavnagar resin appears to have immense potentiality as dechlorinating agent.

4.2.4 Batch Disinfection Studies using Chitin.

Chitin is a biological material obtained from crab shells. It is used for preparing immobilised enzyme columns for treating urea bearing wastewaters (Iyengar, 1978). Preliminary experiments conducted in Environmental Engineering Laboratory at IIT Kanpur revealed that Chitin-glutaraldehyde complex possess significant bactericidal properties. Presence of amino groups on this substance prompted us to try this material in the present study. The adsorption of chlorine onto chitin was less than that of synthetic resins tried above. Moreover, the disinfection data obtained indicate its poor bactericidal performance. This once again makes chitin suitable as dechlorinating agent rather than for disinfection.

From the results presented above it appears that chlorine release is necessary for ensuring destruction of microorganisms. The mechanism then is the usual one where the hydrolysed species of released chlorine act as the active agent of disinfection. The different materials used as supports show that the presence of primary or secondary amide group by itself is insufficient to guarantee chlorine release. What is essential is an easily replaceable atom in the group; in UMF-resin, for example, Cl replaces H to give -NCl, which then hydrolyses to give the active agent, chlorine. Further, the structure of material, i.e., the linkage of various groups, their arrangements etc. may also be important.

4.3 Column Disinfection Studies using UMF-Resin.

After obtaining encouraging results with UMF-resin in batch process, column studies were conducted to evaluate its chlorine releasing and disinfecting ability. Turbid-free test water was used throughout the column studies. Experiments were conducted to find out the effect of different flow rates on chlorine release from the bed, kill of input microorganisms, and exhaustion of the column. The results are presented in the following sections.

4.3.1 Effect of Rate of Flow on Chlorine Release from the Disinfectant Bed.

The chlorine charged resin column was prepared as mentioned in Chapter 3. The column was commissioned by passing test water containing bacteria of the order of 1000 per ml. The loading rate on column was varied between 90 to 1500 lpm/sq.m. The lower value is quite comparable to the loading rate of rapid sand filter. Chlorine release was measured for various intermediate loading rate and simultaneous samples were collected for finding E.coli survivors. Subsequently to evaluate the extent of effectiveness of the disinfectant bed, the column was run at a constant loading rate of 340 lpm/sq.m. which is about 3.5 times higher than that of rapid sand filter. The effluents obtained at this loading rate were found to be free of bacteria until 180 litres of water was passed through the column. However, after passing 180 litres of water the bacterial breakthrough occurred. Further experimentations were carried out at this stage to check the chlorine releasing and the disinfecting behaviour of the column at various loading rates. The data collected were subsequently used. The maximum flow at which the effluent water became once again sterile was 200 lpm/sq.m. for the column which was initially operated at 340 lpm/sq.m. Consequently, the

disinfecting column was again operated at a rate of 100 lpm/sq.m. (equivalent to rapid sand filter rate) and this resulted in the production of additional 50 litres of bacteria free water.

Chlorine releasing pattern of the disinfecting column for various loading rates at the beginning of its operation and after a flow of 180 litres of water through it is presented in Fig. 4.9. It is seen from the figure that chlorine release decreases with the increasing loading rate at both stages of column operation. Apparently this happens because with the increasing loading rates the time of contact between the test water and resin decreases. The mechanism of adsorption of chlorine on the resin certainly has an influence on its release. If the mechanism of chlorine adsorption were of film diffusion type the release of chlorine would have been more with the increasing flow rates (Weber, 1972). As contradictory results are observed in Fig. 4.9, it can be expected that the mechanism of adsorption and desorption of chlorine with UMF-resin is different.

It can also be seen from the figure that for the same flow rate, chlorine release is more at the beginning of the commissioning of column than that after passing 180 litres of water through it. Further, the rate of decrease

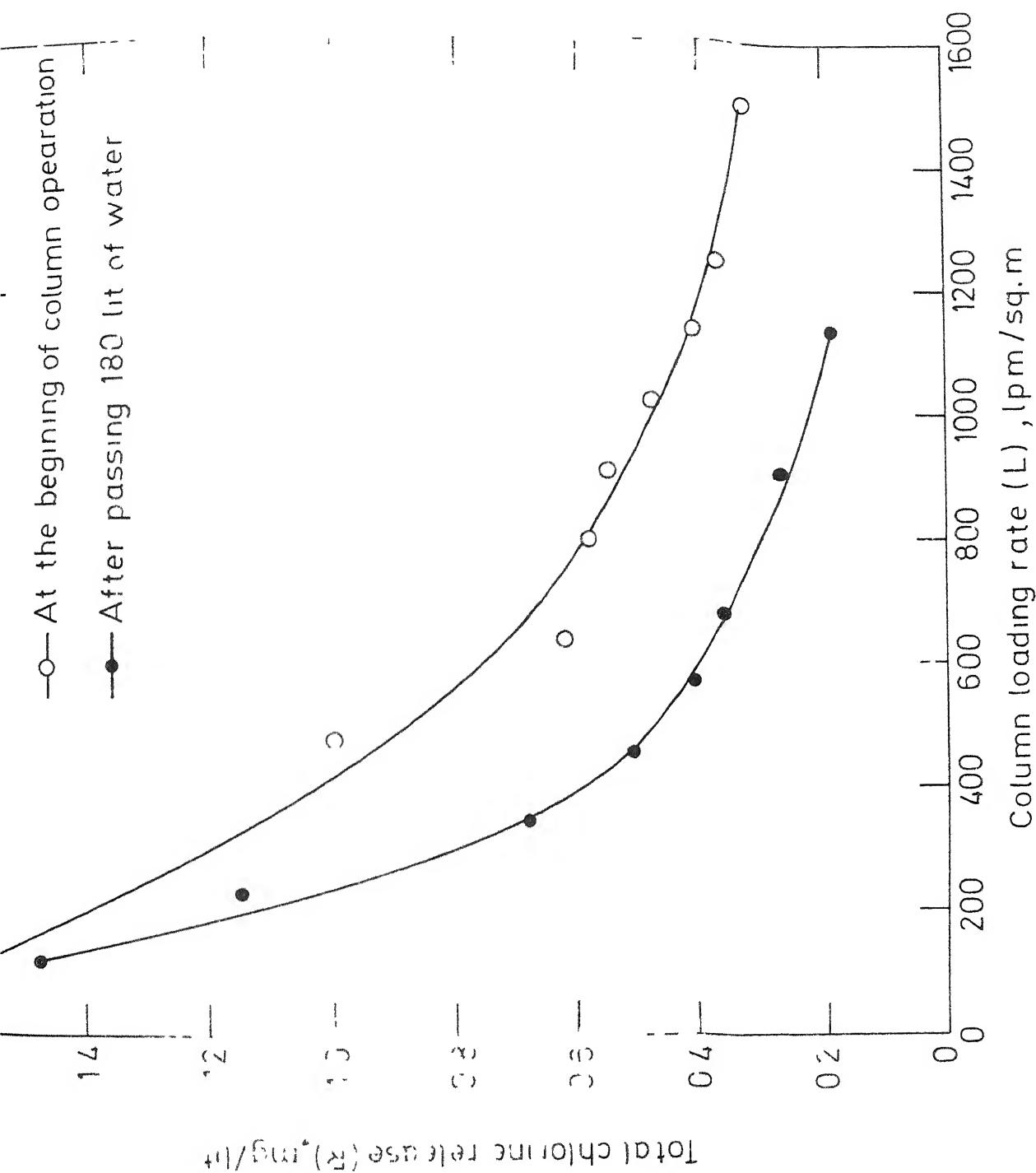
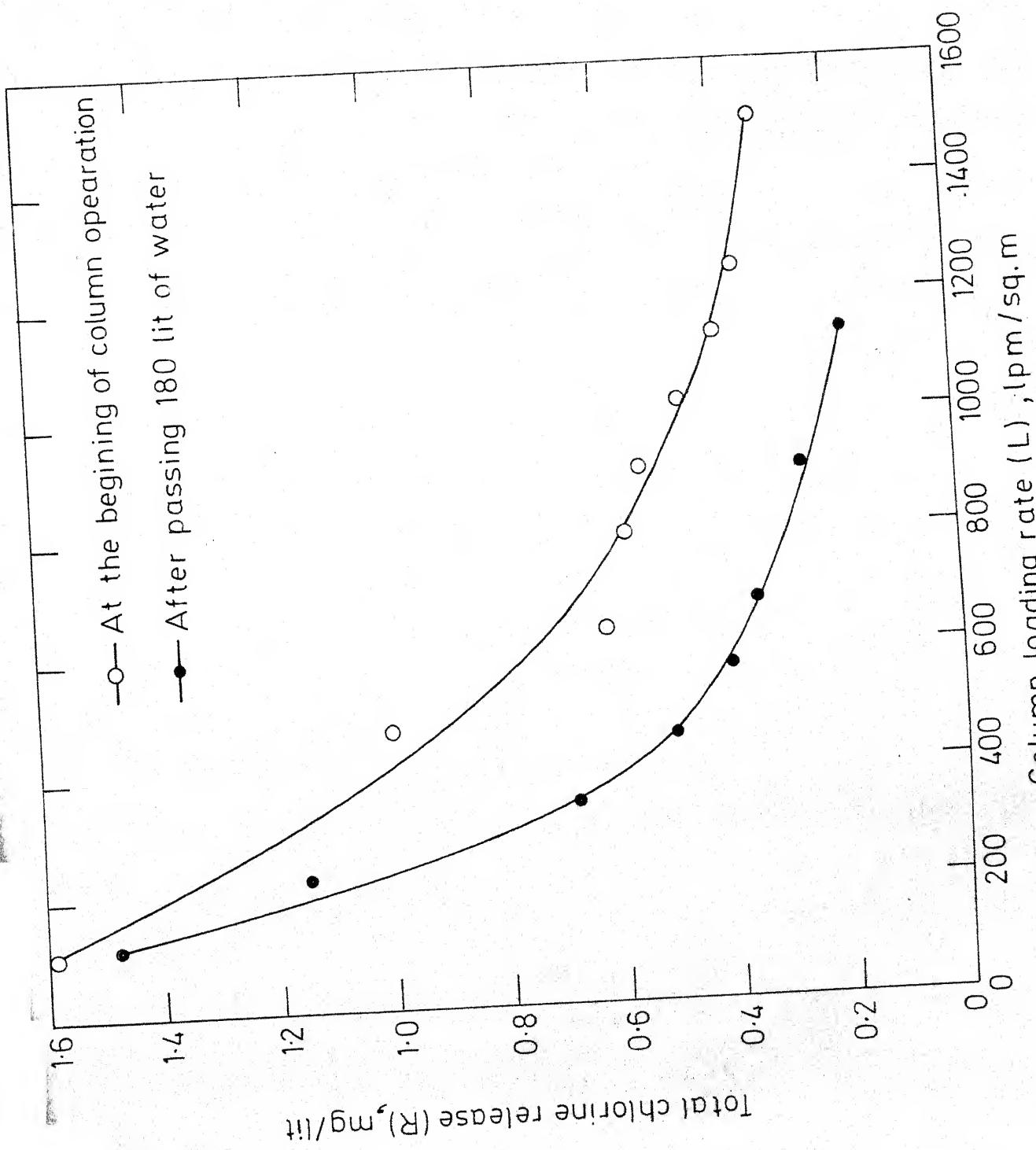


Fig 4.9 Chlorine Release With Loading Rate for UMF-Resin

Fig. 4.9 Chlorine Release With Loading Rate for UMF-Resin
(Column)



D_p = Effective particle diameter

δ = Sphericity of the particle

v_∞ = Approach Velocity

ϵ = Void fraction = $\frac{\text{Volume of voids}}{\text{Total Volume}}$

ρ = Density of the fluid

μ = Dynamic viscosity of the fluid.

Sieve analysis was conducted to determine the effective size of the particle. Based on the sieve opening size, an average diameter of 0.318 mm was considered as effective size of resin particle. The sphericity assumed was 0.75 as reported for grounded material (Fair et.al., 1968).

The voids volume in the bed was measured by filling the column upto the top of resin bed with coloured water and then collecting and measuring the effluent from column till the water level reached the bottom of the bed. The voids fraction thus calculated was 0.3.

The values of Reynold's number calculated at various loading rates varied between 0.65 and 9.42. In porous media the flow is considered laminar upto the Reynold's number value of 2. The transition flow exists for Reynold's number between 2 and 10. In the present investigation the

flow characteristics change from laminar to transition zone with the increasing loading rates. Hence, the flow characteristics in the column appear to influence chlorine release to a certain extent besides the concentration gradient and the contact time.

In order to further understand the nature of the release of chlorine with varying flow rates, it was attempted to linearise the curves obtained in Fig. 4.9. In Fig. 4.10 the linearised plots of the curves are shown. The equation of the lines obtained are as follows ,

$$\ln R = 0.58 - 1.2 \times 10^{-3} L \quad (4.7)$$

$$\ln R = 0.07 - 1.54 \times 10^{-3} L \quad (4.8)$$

where R is chlorine release,mg/l and L is the column loading rate in lpm/sq.m. Equation 4.7 is for chlorine release at the beginning of operation of the column while equation 4.8 indicates chlorine release after passing 180 litres at which breakthrough of bacteria was reported. It can be seen from the graph that to obtain same amount of chlorine in the effluent the column can be operated at comparatively higher loading rates at the beginning of the run than that at the time of exhaustion.

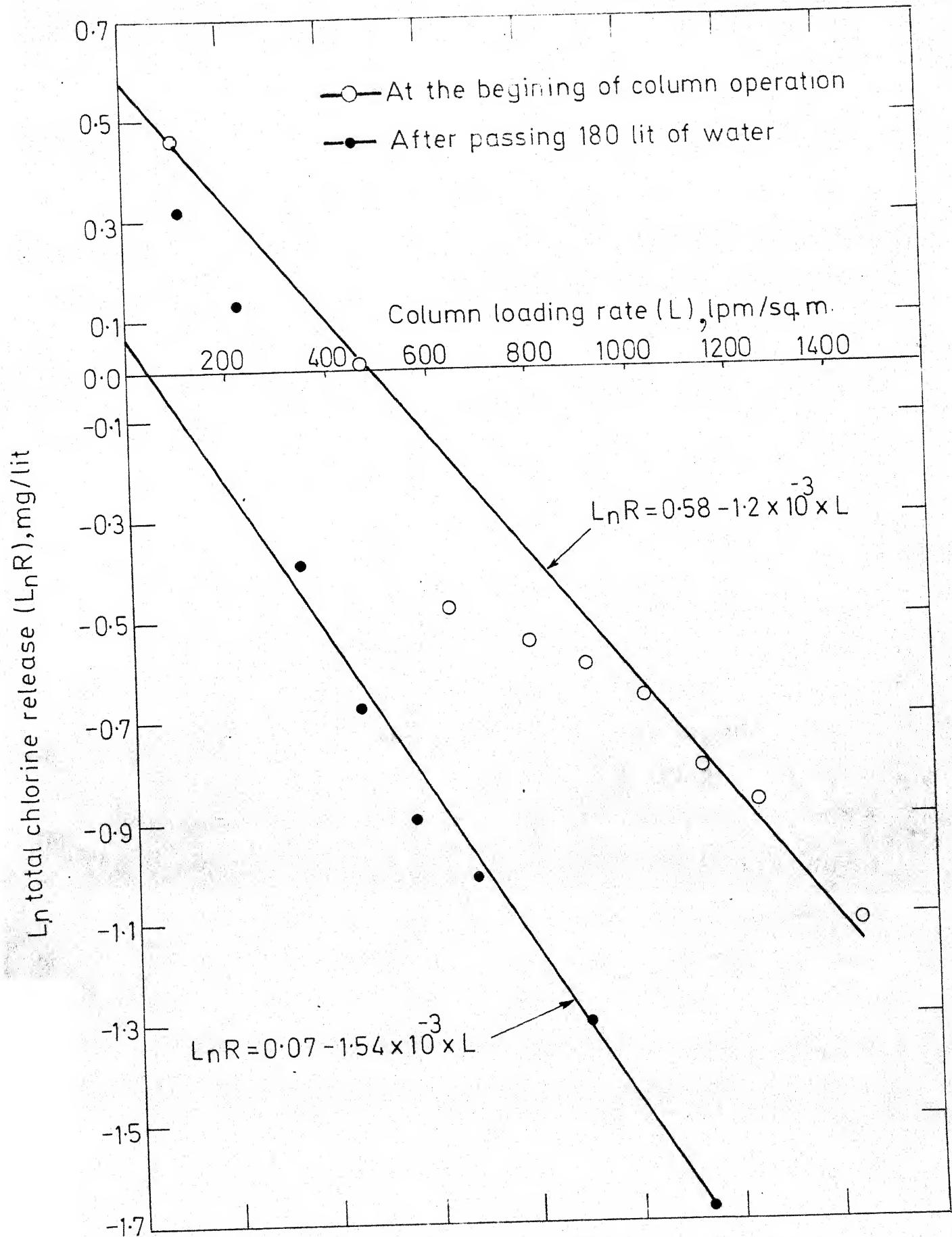


Fig. 410 Linearised Plot for Fig. 4.9

4.3.2 Disinfection Kinetics

In order to design the disinfecting system rationally, it is essential to have a basic understanding of the kinetics of disinfection. The bacterial survivors in the effluent water from the column for various loading rates at the beginning of the commissioning of the column and after passing 180 litres of water were determined as mentioned earlier. The data was analysed according to Chick's model of disinfection and the results are presented in Fig. 4.11. The rate of disinfection is very high ($K = 0.216/\text{sec.}$) initially. After passing 180 litres of water the disinfection rate drops down to $0.021/\text{sec.}$ which is approximately one tenth the value of the initial rate constant. The reason is obvious as after passing 180 litres of water the decreased rate of chlorine release does not yield the same amount of chlorine as in the beginning.

As mentioned in the previous section, the column was operated at a flow rate of $100 \text{ lpm}/\text{sq.m.}$ when breakthrough of bacteria occurred at $340 \text{ lpm}/\text{sq.m.}$ This produced 50 litres of sterile water at a loading rate of $100 \text{ lpm}/\text{sq.m.}$ However, after this breakthrough of bacteria was again observed. At this stage the column was operated at different loading rates and the bacterial number in the effluent was

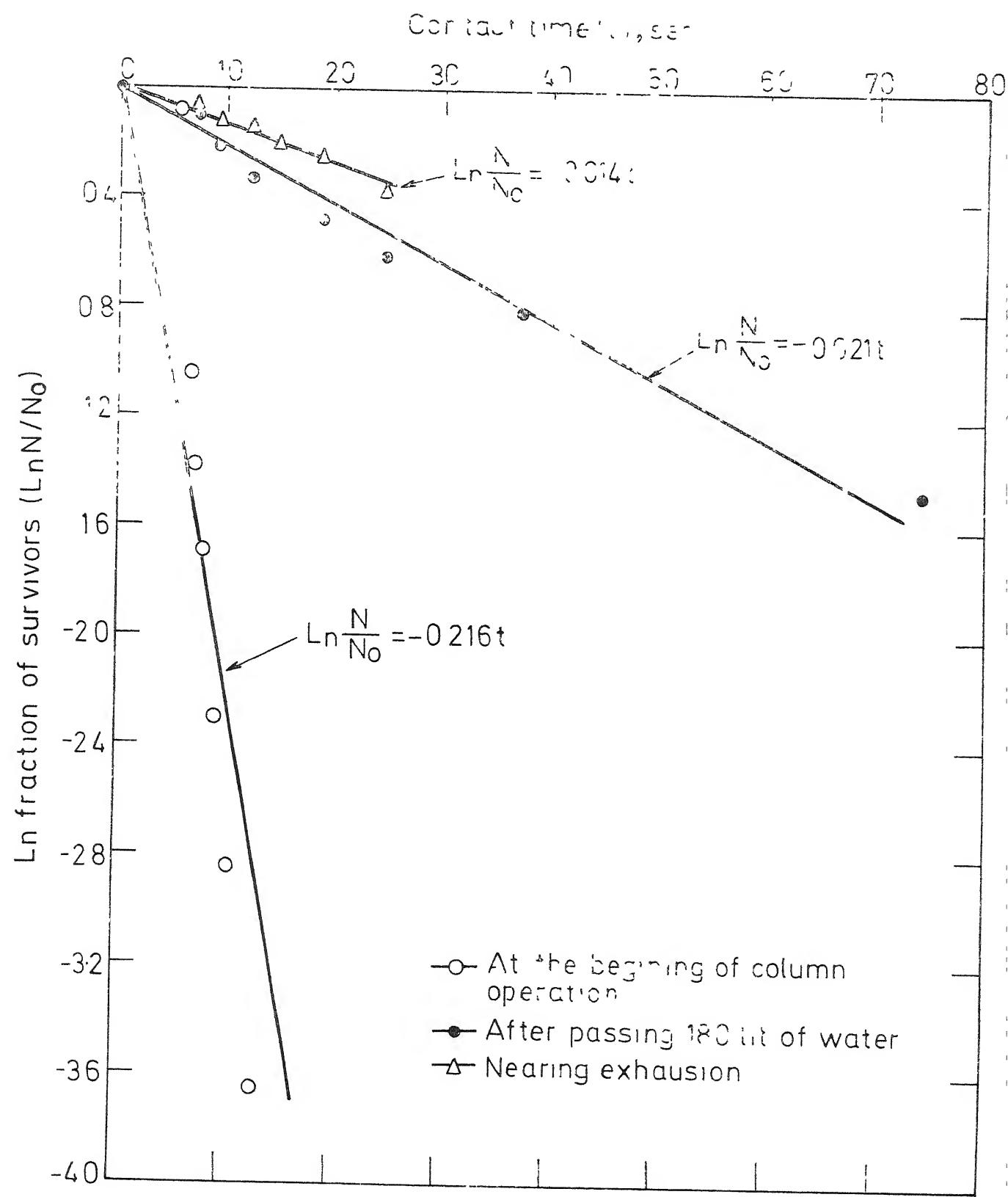


Fig 4.11 Chick's Model for Chlorine Disinfection With UMF-Resin (Column)

enumerated. Fig. 4.11 depicting the Chick's model for this data also shows a disinfection rate constant of 0.014 /sec. which is least among the three. This clearly indicates that the disinfecting efficiency of the column decreases as more and more water is passed through it.

Selleck et.al. (1978) working in the area of disinfection over many years have extensively studied the applicability of the following equation for describing the deactivation of E. coli.

$$S = \left[\frac{Rt}{b} \right]^{-n} \quad \text{when } Rt \geq b \quad (4.9)$$

where S = survival ratio (concentration of bacteria at time t by the concentration at zero time).

R = residual chlorine concentration

t = contact time

b and n are coefficients statistically ascertained.

These investigators proposed that the above equation can be utilised for comparing the efficiencies of alternative disinfection processes. In the present work it was contemplated to test this equation in order to compare the disinfection efficiencies of the column at the beginning and at nearly exhaustion conditions.

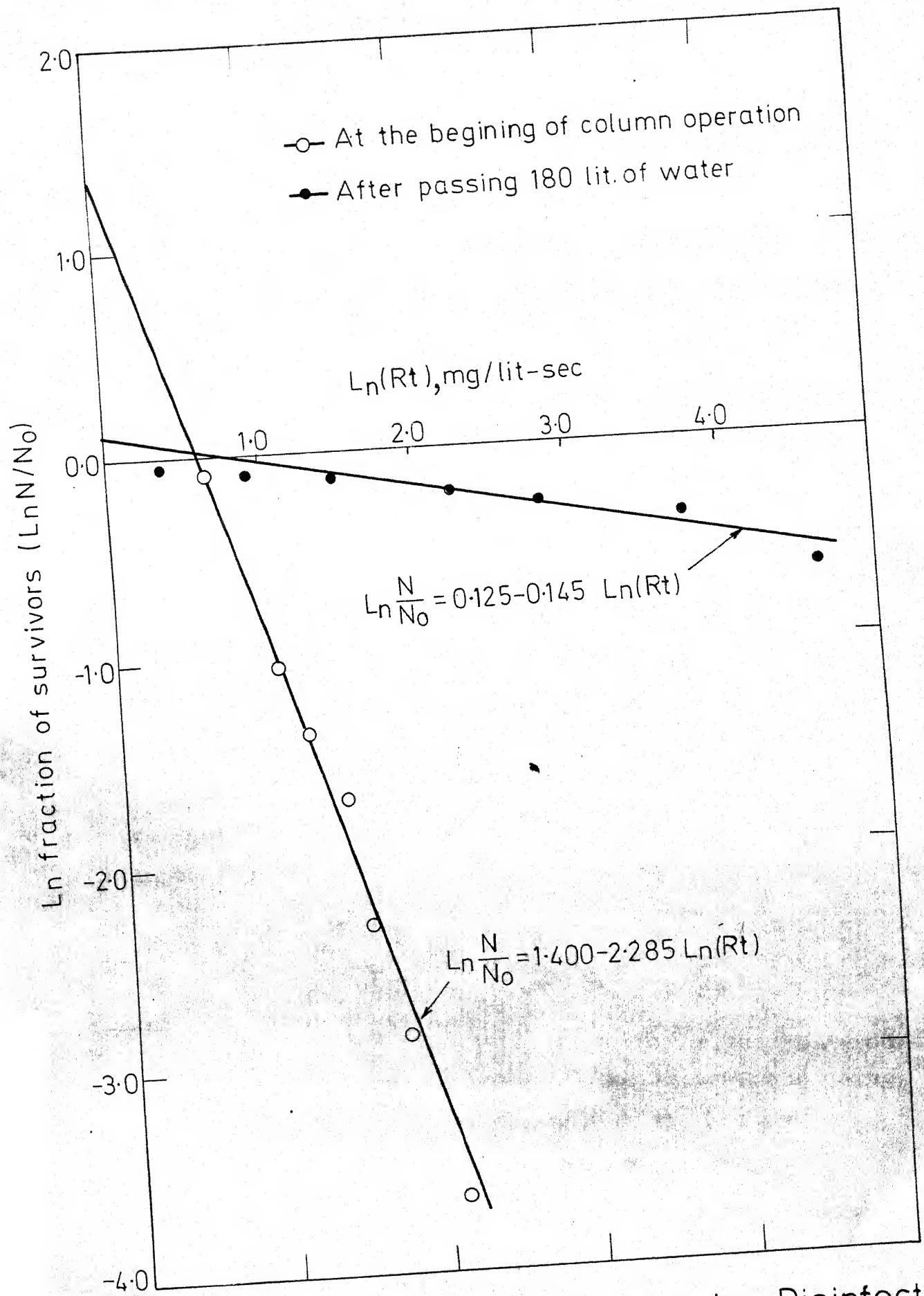


Fig.4.12 Selleck's Model for Chlorine Disinfection

exhaustion the minimum value of R_t (1.4) for a loading rate of 1135 lpm/sq.m. is less than the corresponding value (2.36). All other values of R_t are greater than 2.36. Thus except for one point equation 4.9 is valid for this case also.

In order to obtain a desired fraction of survivors of bacteria say 1 organism/100 ml of water (MPN value accepted for drinking water) the ' R_t ' value for the freshly commissioned column is 1.85 mg/lit-sec. with an input bacterial concentration of 10^5 /100 ml. Depending upon available chlorine concentration the contact time (t) should be either decreased or increased so as to get the above value for R_t . It is evident from the above discussion that both concentration of chlorine and contact time are important in the process of disinfection using fixed bed. Both these factors are also important even in the conventional practice of disinfection by chlorine.

4.3.3 Mechanism of the Action of Disinfecting Column

Based on the bactericidal and chlorine releasing properties of the column it appears that the bed operates successively, in layers, starting from top. At the beginning of column life chlorine released from top few centimeters of the column is enough to disinfect the test water. As the

time and opportunity of contact obtained in this case is maximum(because of the remaining bed lying ahead), the efficiency of column is at its peak. As more water is passed through it the active or effective zone of bed goes down. This reduces the contact time and opportunity between the bacterial cells and the disinfectant, and as a result the performance of bed deteriorates. Perhaps, this is also the reason why the present bed despite its chlorine capacity of 40 mg/ 100 mg is unable to treat that amount of water which the sorbed chlorine would have normally treated if it were added directly to the test water. The probable reason may be that all chlorine adsorbed by present bed may not be in reversible form.

It is expected that once the chlorine is released from the resin the rest of the mechanism of inactivation of bacteria by it is according to any one of the mechanisms or a combination of several mechanisms put forward by various investigators referred in the article 2.3.3.

CHAPTER - 5

SUMMARY AND CONCLUSION

On the basis of the experimental studies conducted the following conclusions may be drawn.

(1) Urea melamine formaldehyde resin adsorbs chlorine reversibly. It readily takes up chlorine from a chlorine rich environment and releases when placed in a chlorine deficient medium.

(2) Strongly basic anion exchange resin (De Acedite-N) supplied by Ion Exchange (India) Ltd. adsorbs chlorine irreversibly. Though there is comparable uptake of chlorine the release of the same is absent. This property might be useful for dechlorinating effluents containing excessive chlorine. Similar observations were also made with the resin obtained from Bhavnagar and chitin.

(3) The disinfection data indicate that the kill of E.coli is due to released chlorine from the bed rather than just by contact between chlorinated resin and bacteria. This explains the success of UH-resin and failure of other resins to disinfect water.

(4) The turbidity tried upto 8 NTU does not seem to interfere with release of chlorine from the resin. However, the disinfection is less due to protection offered

by turbidity to the microorganisms.

(5) The chlorine release from the disinfecting column appears to be a function of flow rates. Higher loading rates exhibit release of lower concentration of chlorine and vice versa.

(6) The disinfection kinetics both in batch and column studies follow the classical Chick's model.

(7) The column can produce sterile water at loading rate of 340 lpm/sq.m which is 3-4 times larger than rapid sand filter. At this flow rate the contact time between contaminated water and chlorinated resin works out to be 25 sec. which is negligible as compared to 30 minutes of contact time provided in the conventional chlorination practice.

(8) When the breakthrough of bacteria started at a flow rate of 340 lpm/sq.m. the column was operated at lower flow rate of 110 lpm/sq.m which again yielded sterile water.

CHAPTER 6

ENGINEERING SIGNIFICANCE

Many difficulties are encountered in disinfecting water in villages, in isolated urban areas and in railway compartments due to lack of special equipments required to dispense and regulate compressed chlorine in water to be treated. Even, if equipments are available the problem of breakdown is very common. In order to eliminate these difficulties, a simple, self regulatory and cheap method of disinfecting water in the form of fixed bed which requires least attention in terms of operation and maintenance has been developed. The present study very clearly indicates that it is possible to use selective resins for adsorbing chlorine which can release the same whenever water is passed through them.

The fixed bed developed using UFF-resin can produce sterile water at a rate of 340 lpm/sq.m which is almost four times more than that of rapid sand filter. The column used in the laboratory containing 1.8 grams of resin charged with 400 mg of chlorine per gram of resin yielded more than 200 litres of sterile water. The treated water always contained residual chlorine of the order of 0.5 to 0.8 mg/l to protect it from post contamination.

Further the disinfecting column can be operated at a lower rate than stated above to get an additional quantity of sterile water.

If the same amount of chlorine as adsorbed by 1.8 g of resin were added directly to the same water having a chlorine demand of 2.5 mg/l, it would have been possible to disinfect not more than 280 litres of water. Accordingly the present system has an efficiency of 70 percent. Assuming the efficiency of conventional chlorination practice to be 75 percent in terms of its handling, dosing and regulating etc., the efficiency of present system is quite comparable. Moreover, the proposed process would eliminate additional chlorine dosing equipment, chlorine storage equipment and regular operation and maintenance of these equipments by skilled operators. Further , the resin once exhausted can be reused for disinfection after chlorine adsorption thus contributing to the overall economy of the system.

CHAPTER 7

SUGGESTIONS FOR FUTURE WORK

Based on the present work and the conclusions drawn, there is a need to conduct further studies in this area considering the great potential of the process particularly in supplying safe water to our rural masses.

1. Many more cheap alternative adsorbents as solid supports should be investigated so as to cut down the cost of the process.
2. The column design might require improvement so as to treat larger quantities of water by regulating the chlorine release.
3. The hydraulics of the resin bed should be more thoroughly investigated.
4. Scientifically the chemistry and mechanism of chlorine release need to be worked out in order to have more insight in the process.
5. The efficiency of disinfecting filter in terms of virus inactivation is to be evaluated.
6. The performance of the chlorine charged resin column in disinfecting treated wastewater needs to be studied.
7. More column studies are required with varying influent turbidity to evaluate the effect of turbidity on the

disinfecting bed performance.

8. The mechanism of kill of bacteria needs to be investigated in such a disinfecting filter.

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